

# SYNTHESIS OF BARIUM SULFATE IN THE VARIATION OF TEMPERATURE AND ADDITIVE CONCENTRATION

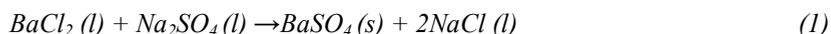
Waleed Ali<sup>1</sup>, Wahyu Putranto<sup>1</sup>, Stefanus Muryanto<sup>1</sup>, and Athanasius Bayuseno<sup>1</sup>

<sup>1</sup>Department of Mechanical Engineering, Faculty of Engineering, Diponegoro University, Tembalang Campus, Semarang 50275, Indonesia

**Abstract.** Barium sulfate (BaSO<sub>4</sub>) with fine sizes is important for many applications. Barium Sulfate (BaSO<sub>4</sub>) is suitable for applications as diverse as whiteness, inertness and high density. Many different approaches have been reported for the preparation of nanoparticles BaSO<sub>4</sub> including the addition of different additives. Aims of this study to synthesize barium sulfate (BaSO<sub>4</sub>) from sodium sulfate and barium chloride with the modification of the mixing speed, temperature and additive concentration variations. This study conducted in Diponegoro University Laboratory. The sample were characterized by a number of different methodologies, including XRD and SEM-EDS. The higher the temperature of the mass of the crust that formed more and more. The results showed a temperature of 40°C was obtained crust mass greater than at 30°C. The addition of the additive citric acid to 20 ppm does not have enough influence to lower the formation of crust mass. From the SEM image, it is clear that the particle size is less than 10 µm.

## 1 Introduction

Synthesis of inorganic powder with ultrafine size, surface properties controlled and controlled morphology attract increasing interest for use are important in many fields. Barium Sulfate (BaSO<sub>4</sub>) is suitable for applications as diverse as whiteness, inertness and high density [1]. Barium sulfate is a kind of important inorganic chemical products as packaging and additives in painting, coating, plastics and pharmaceuticals fiber [2-4]. Barium sulfate crystals can be formed from a chemical reaction as follows:



The reaction liquid / liquid is the primary method of preparation of nano-BaSO<sub>4</sub>. This method has several divisions such as direct rainfall, the separation of micro-emulsion [5] membrane [6], the reactor microchannels [7]. Preparation BaSO<sub>4</sub> particles have been studied to assess the effect of mixing, the model precipitation, the stirrer speed and position feedback on particle size distribution, crystal growth and morphology [8,9].

Many different approaches have been reported for the preparation of nanoparticles BaSO<sub>4</sub> including the addition of different additives [10,11] induction with monolayer and

microemulsion [12]. Addition of additives and induction with LB monolayer can cause significant changes in morphology, but the size is generally within the micron scale than the scale of nanometers. The size and morphology of the corresponding obtained in W / O micro emulsion [13] or reverse micelles approach can be well controlled by adjusting the molar ratio of water to surfactant. However, the results of the product is rather low due to poor solubility of the salt in a conventional micro emulsion. There are also some reports about the preparation of organo-modified BaSO<sub>4</sub>, but BaSO<sub>4</sub> obtained in the micron scale. Although the preparation of BaSO<sub>4</sub> organo capped was previously described, [14] are not suitable conditions for the industry. Preparation of barium sulfate nano particles using tetradecanoic acid, citric acid, heksadekanoat acid and stearic acid as a modifier was studied [2].

When an inorganic filler with surface functional groups reached a polymer matrix, can be expected to improve the stiffness and impact properties simultaneously [1]. However, the surface of the inorganic particles (eg, BaSO<sub>4</sub>) is hydrophilic, so it is not easy to disperse these particles in a lipophilic matrix. For this reason, it is important to modify the surface of BaSO<sub>4</sub>. One of the few ways to achieve good dispersivitas is to modify the surface hydrophilic particles so that the lipophilic nature. For the purpose of these various coupling agents, who are able to introduce specific functional groups to the surface of the particles, have been used titanate coupling agent, silane coupling agents and organophosphonic acid [15]. Aims of this study to synthesize barium sulfate (BaSO<sub>4</sub>) from natrium sulfate and barium chloride with the modification of the mixing speed, temperature and additive concentration variations.

## **2 Material and Method**

### **2.1 Chemicals and instruments**

The starting material used in this study are Barium chloride, sodium sulphate and citric acid. They are used without further purification. Barium sulfate is characterized by using X-ray Diffraction (XRD) patterns recorded on a diffractometer XRD BaSO<sub>4</sub> and SEM-EDS.

### **2.2 Sample preparation**

Direct precipitation (DP) Procedure: 4.447 g barium chloride (BaCl<sub>2</sub>) was added to 1000 ml H<sub>2</sub>O and 2.585 g of sodium sulfate (NaSO<sub>4</sub>) was added to 1000 ml H<sub>2</sub>O and added citric acid as an additive in various concentrations (5 and 20 ppm), Drogpwise solution was added into the flask while stirring at room temperature with mechanical stirring strong dispersant at 200 rpm. Steady drop rate is 20 drops min<sup>-1</sup>. The precipitate is separated from the mother liquor by centrifuging at 3000 rpm for 20 minutes. And then the supernatant solution was discarded and the solid redispersed in deionized water. This process is repeated three times to rinse particles. After the last centrifugation, the precipitated particles are dried in a microwave oven with a temperature varying 30 and 40°C.

## **3 Result and Discussion**

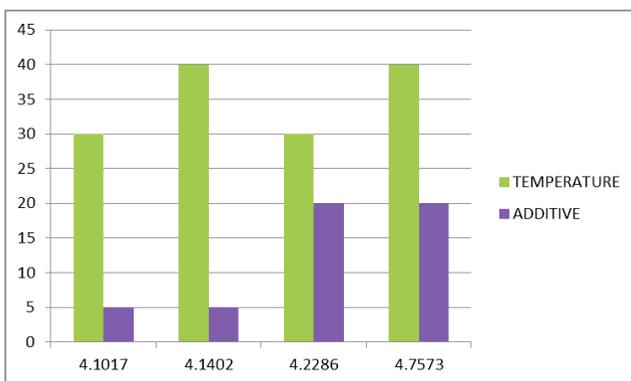
### **3.1 X-ray Diffraction**

XRD test to prove that the scale of the research result was really the barium sulfate (BaSO<sub>4</sub>) scale Figure 1 shows the XRD patterns of barium sulfate. This shows that

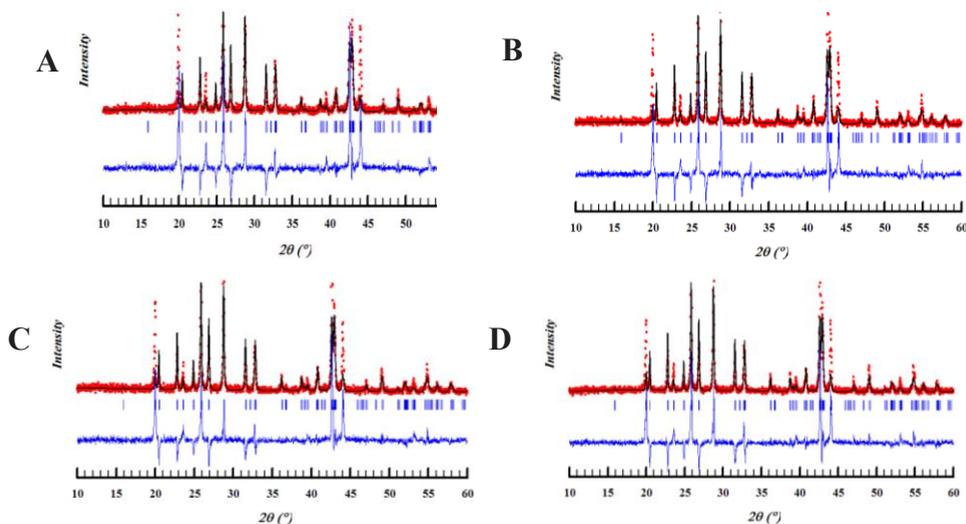
nanoscale barium sulfate is mainly composed of barite. All peaks can be indexed as orthorhombic structure typical BaSO<sub>4</sub>, with crystalline cell constants  $a = 7.144 \text{ \AA}$ ,  $b = 8.865 \text{ \AA}$ ,  $c = 5.445 \text{ \AA}$ , which is basically in accordance with the reported values (JCPDS No. 80-0512) [2]. Crystal size of the sample estimated from XRD peak line widths.

Identification of the powder as a phase-burnt and calcined done using XRD. Average crystal size of the powder was measured by X-ray line-extension technique using Scherrer formula BaSO<sub>4</sub> XRD patterns of nano powders prepared at different calcination treatment is shown in Figure 1.

In this study we have been exposed to nanoparticles of barium sulfate (BaSO<sub>4</sub>) of sodium sulphate and barium chloride with variations in temperature and concentration of additives. The more the concentration of additive affects the particle size increases. Results were different from the research conducted [16] showed that the polymaleic acid with a concentration of 4 ppm is able to reduce the formation of CaSO<sub>4</sub> crust on process and growth.



**Fig. 1.** The XRD pattern of particle in different crystallography orientation at different temperature and concentration additive



**Fig. 2.** XRD patterns of nanocrystalline BaSO<sub>4</sub> at different temperature and concentration additive (A : 30°C and 5 ppm ; B : 30°C and 20 ppm ; C : 40°C and 5 ppm ; D : 30°C and 20 ppm)

The addition of additives was able to suppress the formation of vaterite so the crust that dominates the form of calcite [13]. The use of additives for substances that are very complex, very important in adjusting the crystal habit and purity, when low concentrations it will affect the kinetic nucleation and crystal growth. It is assumed that the additive serves to inhibit crystal growth by slowing the rate of crystal growth, increasing the heterogeneous nucleation, control and stabilize precipitation polymorph. This affects a number of additives in salt deposition related to adsorption on the surface. One way to prevent a crust that is by keeping the anion-cation forming the crust remains in the solution. Scale inhibitor is a chemical that serves to keep the crust-forming anion-cation remains in the solution, so expect no precipitation occurs [17].

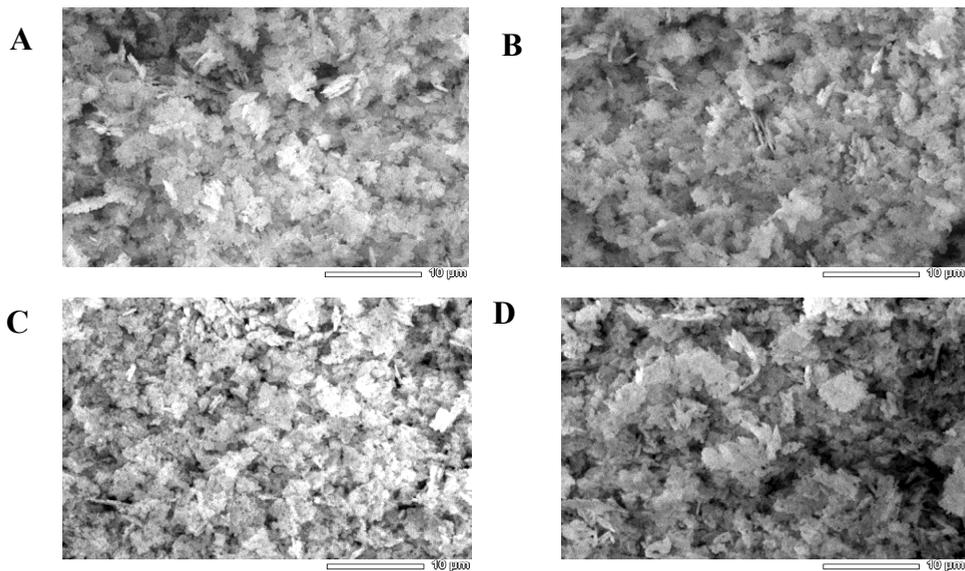
Figures 2. (a, b, c, and d) represent the formation of BaSO<sub>4</sub> crust at different temperatures of 30 and 40°C with the addition of the same additive at the same concentration (5 ppm and 20 ppm). The crust precipitates of BaSO<sub>4</sub> have ions which is solid and has a tendency to form crust precipitates as well as calcium sulfate (CaCO<sub>3</sub>), gypsum or calcium sulphate (CaSO<sub>4</sub>.2H<sub>2</sub>O). The formed crust is included in the type of hard scale that has the brightest primary properties, and if there is impurities (oil or iron oxide) it will become rather dark and almost insoluble in acid. BaSO<sub>4</sub> crust precipitates are generally formed in oil fields whose processes are affected by changes in pressure, temperature and dissolved salts. Results were different from the research conducted showed that the polymaleic acid with a concentration of 4 ppm is able to reduce the formation of CaSO<sub>4</sub> crust on process and growth [16].

### 3.2 SEM-EDS

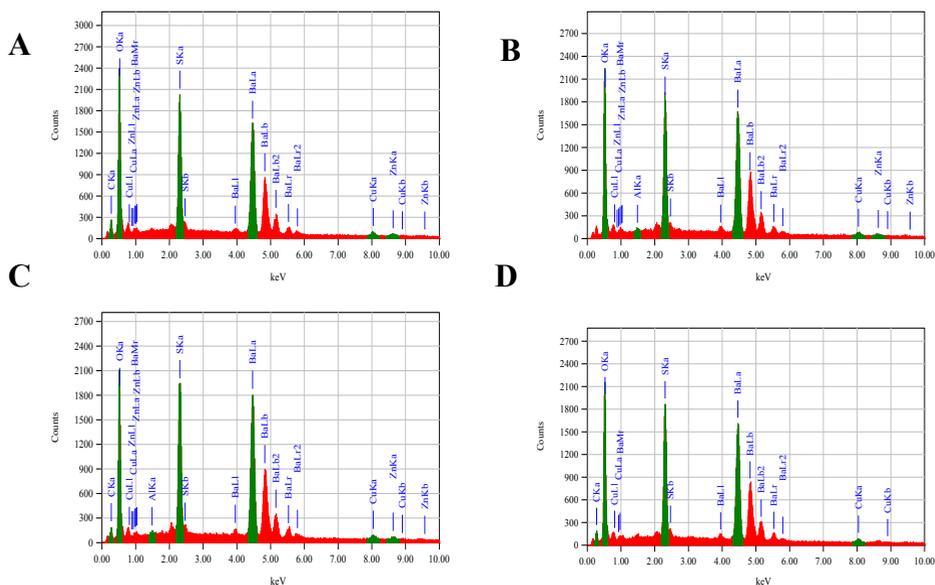
The SEM (Scanning electron microscopy) test was conducted to examine the crystal morphology while the microanalyser test (EDS) was aimed to find out the crystal composition and. SEM was used to analyze the morphology and size of the synthesized BaSO<sub>4</sub> particles [18]. Water content greatly affects the shape of BaSO<sub>4</sub> particles. When the water content is maximal, cubic particles can be obtained.

Figure 3.(a, b, c, and d) are the result of crystallization test BaSO<sub>4</sub> particles with adding additive. The photos show that the crystal are approximately same, in plate like form. Gypsum phase of the barium sulfate scale has a monoclinic crystal form. Monoclin is a characteristic feature of the BaSO<sub>4</sub> crystal form. Referring to the crystal system, the crystal system has different rib lengths ( $a \neq b \neq c$ ), and angles  $\alpha = \gamma = 90^\circ$  and  $\beta \neq 90^\circ$ . The shape of a flat-shaped crystal BaSO<sub>4</sub> resembles a board shape, in which the width is thick not too far away.

From the results of the SEM test BaSO<sub>4</sub> particles indicates that the addition of a larger additive can suppress the formation of calcite / monoclinic phase which is a type of hardscale phase. When these crystals form and settle in the pipes it will produce a crust that is difficult to clean from a piping system. While the other two types of crystals, namely aragonite and vaterite, is a type of softscale that is easier to clean when attached to the wall in the pipe [19].



**Fig. 3.** The SEM image of the Barium sulphate nanoparticles at different temperature and concentration additive (A : 30°C and 5 ppm ; B : 30°C and 20 ppm ; C : 40°C and 5 ppm ; D : 30°C and 20 ppm)



**Fig. 4.** The EDS spectrum of the Barium sulphate nanoparticles at different temperature and concentration additive (A : 30°C and 5 ppm ; B : 30°C and 20 ppm ; C : 40°C and 5 ppm ; D : 30°C and 20 ppm)

Figure 4 shows the energy dispersive spectrum of the BaSO<sub>4</sub> particles with additive citric acids which clearly show the presence of C, O, S, Cu, Zn, and Ba elements. The results of the study did not show any citric acid particle in EDX pattern. This is because the addition of citric acid is too little. Meanwhile, there are Cu and Zn in the EDX pattern. Maybe Cu and Zn were released from the container used for crystallization. Cu and Zn derive from the product of corrosion.

## 4 Conclusion and Remarks

The higher the mass of the crust is formed more and more. The result shows a temperature of 40° C obtained by crust mass greater than 30° C. In addition of 5 ppm additive, crust mass at temperature 30° C is 4.1017 gr while at temperature 40° C is 4.1402 gr. In addition of 20 ppm additive, the crust at 30° C is 4.2286 gr and at 40° C is 4.7573 gr. Based on these results it is evident that the addition of citric acid as an additive to 20 ppm does not have enough effect to decrease the mass formation of the crust. From the SEM image, it is clear that the particle size is less than 10 µm. BaSO<sub>4</sub> particle dispersive spectrum with added citric acid, which clearly indicates the presence of C, O, S, Cu, Zn, and Ba elements. The absence of citric acid seen in the EDX pattern is due to the use of too little citric acid. While the presence of Cu and Zn should not exist, it is possible to contaminate Cu and Zn on the containers used in crystalline formation.

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