



The Role of Additives on the Barium Sulphate Crystallization

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In the present study, synthesis of barium sulfate crystals (BaSO₄, barite) is carried out by chemical precipitation method to investigate the effects of polystyrene and alginate on particle size and morphology of crystals. As a second step of this research, the spontaneous precipitation of barite at 25 °C was investigated in the presence of polyacrylic acid (PAA), polyvinyl sulphonic acid (PVS) and polyethylene glycol (PEG). The degree of inhibition is measured as the reduction in initial crystallization rate, determined by conductivity of the crystallizing solution. SEM analysis of the crystals was made to determine the particle size and the morphology. The results have shown that the additives, used in this study, were effective in order to minimizing the particle size of the crystals and reducing the crystallization speed of barium sulfate.

Keywords: Crystallization, barium sulfate, additives, particle size, morphology

Introduction

Since it is a very important inorganic compound that is mainly used in the petrol industry but in other industries like paint and pharmaceutical as well, crystallization of barium sulfate has attracted a great deal of attention in recent years¹⁻³. The researchers focused especially on controlling crystal size and morphology using additives. With the addition of additives at very low concentration, it is possible to obtain crystals ranging from micro size to nanosize in order to use in many industrial production like chemicals, catalysts, medicine, cosmetics, pigments, etc⁴⁻⁶. The adsorption of these species to crystal surface strongly depend on their structure such as nature of their functional groups, molecular weight and chemical composition^{7,8}.

Precipitation of barite cause scaling problem in the processing equipment of many industries. For instance, formation of barium sulfate crystals in offshore oil and gas production lead to a decrease in heat transfer

rate and increasing operating cost. Therefore, inhibiting barium sulfate scales has economic impact^{9,10}.

Nano sized barium sulfate production or decrease the size of precipitates to nano could be formed by breaking down processes such as grinding or by synthesis methods like reaction and precipitation. There are also some researches made with organic and inorganic additives to produce nanoparticles^{11,12}.

In this study, the evaluation of the polymers (PAA, PVS and PEG) for inhibiting barite growth was examined using the chemical precipitation method. Chemical precipitation, one of the effective method to produce barite crystals, mostly preferred to understand the nucleation and growth mechanism of crystals⁹. Also, we used polystyrene and alginate to minimize the particle size of barium sulfate crystals.

Experimental

Materials

Barium chloride dehydrate (99%) and

sodium hydroxide were bought from J.T. Baker, sodium sulfate (99%), polyvinylsulphonic acid and polystyrene were purchased from Sigma-Aldrich, hydrochloric acid was obtained from Merck, alginate was supplied from Protonal, polyacrylic acid was bought from Acros Organics, polyethyleneglycol was obtained from BASF and no any further purification was made to the chemicals. Double distilled water is used in all experiments.

Methods

Barium chloride and sodium hydroxide were taken in equal volume (100 ml) and equal molarity (0.1M). The pH level of the reactor was controlled by HCl and NaOH to stabilize at pH 6. Temperature and pH of the mixture was measured with a probe. The first experiment was made without additives to observe the difference with the experiments which they have made with additives. Polystyrene and alginate were used in 0.001M. The crystallization of barium sulfate was carried out in a double-walled reactor at 30 °C. The solution that contains barium sulfate crystals was taken and transferred into small tubes in order to make centrifuge. The centrifuge was made 3 times and then the crystals were collected. As a final step the crystals were put in a baker at 110 °C for one day. Then, the crystals were examined by scanning electron microscopy (SEM) (JEOL JSM-SEM), FT-IR (PerkinElmer Spectrum 100) and X-ray diffraction (XRD) (Panalytical X'pert Pro PW 3040/60).

The second part of study, the supersaturated solutions for growth experiments were prepared by the slow mixing of equal molar solutions of barium chloride and sodium sulfate. The temperature was fixed at 25 °C. PAA, PVS, PEG were added in 0.1

ppm, 0.5 ppm, 1 ppm, 2 ppm. The crystallization was carried out in a double-walled reactor. Conductivity of the solution was measured and the data were recorded by the computer. The graphics were drawn on the computer based on the gathered data. The effect of polymers on the rate of precipitation of BaSO₄ was determined by recording the decrease, as a function of time, in conductivity of a solution. The ratio of the rate of crystallization of the pure solution (k_0) to the rate of crystallization in the presence of additive (k) showed the effectiveness of the additives. The higher k_0/k values correspond to a better inhibition.

Results and discussion

The crystals were characterized by using scanning electron microscope (SEM), scanning electron microscopy, X-ray diffraction, and Fourier transform infrared resonance techniques (FT-IR). Identification of functional groups present in the pure BaSO₄ particles was identified by FT-IR spectra as shown in Fig.1. All peaks of the spectra confirm that the material is barium sulfate. X-ray diffraction patterns of bulk barite crystals are shown in Fig.2. FT-IR and XRD confirms that the material is barium sulfate. The hkl values of BaSO₄ crystals are (101), (111), (200), (021), (210), (121), (211), (002), (220), (400), (140), (330), (041) and (142). When compared the data with literature, the diffraction lines agree with the orthorhombic structure of BaSO₄ crystals¹³.

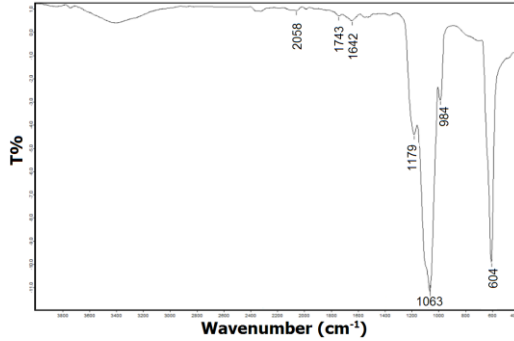


Fig.1. FT-IR spectra of images of pure barium sulfate.

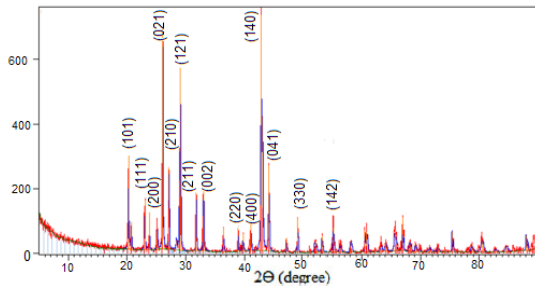


Fig.2. XRD patterns of BaSO₄ particles

We investigated the crystal size and morphology change of barium sulfate in the first part of our study according to the additives that we have used. As a first step of the experiments, barium sulfate crystallization was made without additives and then SEM pictures have been taken. The SEM results are given in Fig. 3. The crystal sizes were measured at a minimum of 100 crystals from the SEM results. The results have shown that the crystals, obtained without additives, had irregular shapes, which were called platelet-like crystals (Fig.3a). Also the crystals were far away from being spherical. The average size of the crystals has been found as 0.32 μ m width and 0.60 μ m length. The first additive, polystyrene was used at 0.001M concentration, 25 °C and pH 6. The SEM images have been taken and the crystal sizes have been measured. The average size of the crystals has been found as 0.29 μ m width and 0.51 μ m length. Also the

crystal morphology was very close to the crystals which have been made in the absence of additives. The last additive alginate was used at 0.001M concentration, 25 °C and pH 6. The SEM images have been taken and the crystal sizes have been measured. The average size of the crystals has been found as 0.28 μ m width and 0.54 μ m length. The shape of the crystals was like rice-shape crystals and the crystals have been piled together. The average sizes of barium sulfate crystals are summarized in Fig.4.

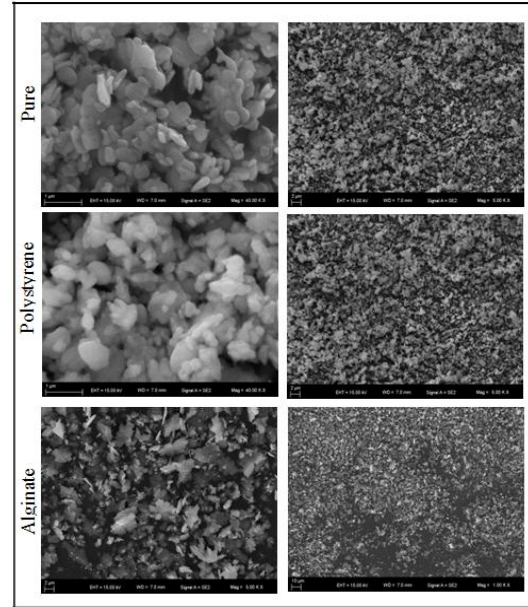


Fig.3. SEM images of barium sulfate with different additives

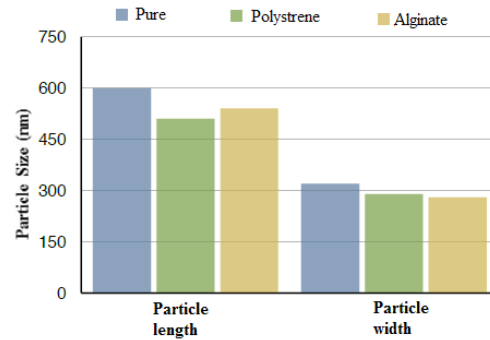


Fig.4. The average sizes of barium sulfate crystals

As a second part of the experiment, we investigated the reduction of the barium sulfate crystallization speed. In the light of the other experiments in the literature⁴⁻⁹, we know that additives are highly effective to slow down the crystallization. Additionally, additives which they belong to polymer group, they are efficiently than the other additives. We have chosen PEG, PAA and PVS as the additives and they were used in concentrations of 0.1 ppm, 0.5 ppm, 1 ppm and 2 ppm. The crystallization of barium sulfate in the absence of additives was made and the conductivity data have been recorded. According to the data, the graph was drawn and the slope (k_0) was found as 2.96. The graph is given in Fig.5. The crystallization experiments have been made with the additives and each slope of the graph compared with k_0 .

Table 1 gives the summary of the experimental k and k_0 values determined from the initial slope of the conductivity curves. As shown in Table 1 all polymers are reasonably good growth inhibitors. The experimental results in the present study show that k_0/k ratio increases with increasing additive concentration. In the presence of polymer the crystallization reaction begins immediately; there is no induction effect.

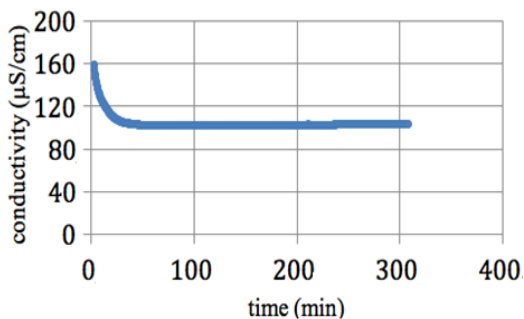


Fig. 5 Conductivity-time graph of pure BaSO₄ crystallization

Table 1. Comparison between k_0/k values in different additive concentrations

Additive concentration (ppm)	PAA	PVS	PEG
	k_0/k	k_0/k	k_0/k
0.1	1.12	1.67	1.35
0.5	1.27	1.71	1.53
1	1.35	1.92	1.90
2	1.47	2.07	2.18

There have been many researches due to the additives that are directly affected to the growth size and morphology of the crystals. The growth of a crystal can be blocked or reduced by an additive which used as an inhibitor. As a further approval, kinetic results can be applied to adsorption models such as Langmuir, Temkin, etc. In this study, we fit the data into Langmuir adsorption model to figure out how much the results are acceptable by the adsorption theory. As long as the graph has linearity, it can be said that it suits to Langmuir adsorption theory¹⁴. Langmuir adsorption can be expressed with Eq. 1

$$\frac{k_0}{k_0 - k_i} = 1 + \frac{1}{K_{aff} C_i} \quad (1)$$

Where;

k_0 = crystallization speed without additive

k_i = crystallization speed with additive

K_{aff} = Langmuir affinity constant

C_i = polymer concentration

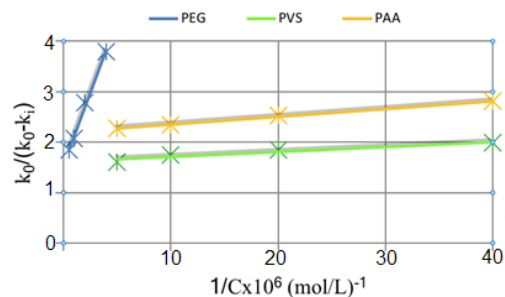


Fig. 6. Langmuir adsorption model

Table 2. Langmuir affinity constants for the crystallization of barium sulfate

	$K_{\text{aff}} (10^7)$	R^2
PAA	9.2	0.99
PEG	0.18	0.99
PVS	6.5	0.92

The graph was illustrated in Figure 6 and drawn between $k_0/(k_0-k_i)$ and $1/C_i$ to find out the affinity constant which is the slope of the graph. The higher k_{aff} indicates the higher effect of the additive in the crystallization speed reduction and blocking the growth size of the crystal. K_{aff} values are given in Table 2. As it seen from the graph, all the three lines are linear and high R^2 results shows the linearity. Thus, it can be said that Langmuir adsorption model is an appropriate model for the additives.

Conclusions

It was found out that, additives in low concentrations were effective to reducing the particle size. Polystyrene was a better additive in decreasing the crystal size than alginate. Morphology of the particles didn't changed significantly in the presence of additives. The second part of the research showed that, polymer based additives were effected in decreasing the speed of barium sulfate crystallization. All results were fit to Langmuir adsorption model and the K_{aff} values have shown that PAA is the most effective additive to inhinite the barium sulfate crystallization. PEG was the least effective additive in all three additives.

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