Research Article

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Influence of cationic surfactants on the growth of gypsum crystals

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Abstract: The effect of cationic surfactants on the growth of gypsum was evaluated under conditions of a simulated production process of gypsum desulfurization. We used a laser particle size analyzer and a microscope to determine the particle size and morphology. The growth rate of gypsum was determined by the equation for the rate of chemical reaction of $CaSO_4 \cdot 2H_2O$. The results showed that the growth rate at a supersaturation ratio of 2.4 increased by 50% with 30 mg/L of a dodecyldimethylbenzylammonium chloride. The gypsum morphology changed from needle-like in the absence of additives to tabular in the presence of cationic surfactants, indicating that relatively thicker and larger crystals were formed. Finally, the investigated cationic surfactants were beneficial to the normal operation of the desulfurization process.

Keywords: crystal growth, gypsum, cationic surfactants

1 Introduction

To save water, thermal power plants have begun to implement zero-discharge measures for the entire plant. The reason for the implementation of zero-discharge of wastewater in entire plants is the large amount of water rich in chlorine and salt in coal-fired power plants, which enters the desulfurization system, bringing in impurities and affecting the crystallization characteristics of desulfurized gypsum [1–3]. Current gypsum desulfurization in coal-fired power plants faces problems of stickiness on the surface of gypsum and “thinning” of gypsum dehydration, which affects the safe operation of the desulfurization system and also has a negative impact on the resource utilization of desulfurization gypsum.

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Cationic surfactants are frequently used to kill bacteria in the circulating water systems of thermal power plants. The concentration of cationic surfactants in the wastewater from circulating cooling water increases in the desulfurization system over time because of the zero-discharge of wastewater in the entire plant.

Crystal growth of $CaSO_4 \cdot 2H_2O$ have been extensively studied using pure calcium chloride and sodium sulfate solutions to simulate the gypsum crystallization process [4–11]. Surfactants are expected to influence the growth rate of gypsum crystals, which directly impacts the dewatering properties of gypsum [4]. The presence of surfactants reduces the hydration of calcium ions, and larger crystals with a low surface area can be produced in the presence of surfactants [5]. A small amount of soluble impurities (from the used surfactant) altered the growth rate and crystal habits of the formed crystals. El-Shall *et al.* [11] reported that a cationic surfactant (cetyltrimethylammonium bromide) increased the growth efficiency. The growth rate and particle size of gypsum were increased by cetylpyridinium chloride addition [5]. The flue gas desulfurization gypsum crystallization process may be affected by the presence of cationic surfactants.

At present, there are several studies only on the effect of cationic surfactants on the growth of gypsum under wet desulfurization conditions. In this study, by using calcium chloride and sodium sulfate solutions to simulate gypsum growth experiments, we studied the growth of gypsum in a synthetic saline NaCl solution with and without dodecyldimethylbenzylammonium chloride (DDBAC) and 5-chloro-2-methyl-4-isothiazolin-3-one (CMI). The growth rate of gypsum was calculated by first-order reaction kinetics [12]. It provided guidance for the safe and stable operation of a desulfurization system under the conditions of zero-discharge of wastewater in the entire plant.

2 Experiment

2.1 Materials

Calcium chloride and sodium sulfate produced by Tianjin Zhiyuan Chemical Reagent Company in China were used to prepare different calcium sulfate supersaturated solutions. Two cationic surfactants were used – DDBAC and CMI (Beijing, China).

2.2 Procedure

2.2.1 Reaction and crystallization

500 mL of deionized water was heated to 50°C in a 1,000 mL LOIKAWa three-neck bottle using a temperature-controlled water bath. Two 250 mL solutions of $CaCl_2$ and Na_2SO_4 in equimolar concentrations and the desired amounts of cationic surfactant solution were added gradually to the heated deionized water. The reaction was maintained at 50°C with constant agitation at 150 rpm at pH 5. These conditions simulate the process of desulfurized gypsum produced by wet desulfurization in thermal power plants.

2.2.2 Conductivity measurements

The conductivity of the resulting solution was measured at different time intervals during the reaction using a MIK-EC8.0 conductivity meter. Each experiment was repeated three times, and the average results were presented.

2.2.3 Crystal size distribution

At the end of the experiment, the formed gypsum was separated to analyze the crystal size distribution. About 5 mL of the reaction mixture was dispersed in about 50 mL of ethanol, and the size distribution was determined using a laser particle size analyzer (WinnerZD2000, China).

2.2.4 Gypsum morphology

The filtered gypsum was first washed with saturated solution and then with ethanol for microscopic examination. A scanning electron microscope (SEM) (REGULUS8100, Hitachi, Japan) was used for the investigation of crystal morphology.

2.3 Growth rate calculation

Crystals can be analyzed as a set of clusters with strong bonds formed in the early stages of molecular association. The crystal structure in these cases can be represented as a series of kinetically controlled events.

Based on the chemical reaction kinetics, the growth rate of gypsum can be expressed by the first-order reaction rate equation as follows:

$$-\frac{\mathrm{d}c}{\mathrm{d}t} = kc.$$

Integration of the above formula gives

$$c = c_0 \mathrm{e}^{-K_1 t}$$
$$\ln c = \ln c_0 - K_1 t,$$

where c_0 (mol/L) is the initial ion concentration in the solution, t is the reaction time (min), c (mol/L) is the ion concentration in the solution after time t, and K_1 (min^{-1}) is the reaction rate constant of crystal growth.

3 Results and discussion

The formation of crystals can be briefly summarized in four parts. First, a supersaturated solution is produced. Second, clusters are formed by intermolecular interactions, and then crystal nuclei are produced from the formed clusters. Finally, the crystal nucleus further grows into a crystal. The formation process of gypsum can be represented by the following reactions:

$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4$ supersaturated solution

$CaSO_4$ supersaturated solution + $H_2O \rightarrow CaSO_4{\cdot}2H_2O$ clusters

$CaSO_4{\cdot}2H_2O$ clusters $\rightarrow CaSO_4{\cdot}2H_2O$ crystal nucleus

$CaSO_4{\cdot}2H_2O$ crystal nucleus $\rightarrow CaSO_4{\cdot}2H_2O$ crystal

Two common concentrations of cationic surfactants were 30 and 50 mg/L in the desulfurization system of thermal power plants. The growth of gypsum was studied with and without cationic surfactants in 30 or 50 mg/L concentrations. Two cationic surfactants, DDBAC and CMI, were used, and the effect of these additives on gypsum growth was evaluated.

3.1 Effect of cationic surfactants on the crystal size of gypsum

The particle size of the samples obtained in the experiment was measured using a laser particle size analyzer. The results of the gypsum particle size at a supersaturation ratio of 2.4 with and without cationic surfactants are given in Table 1, showing that the presence of surfactants yields a higher particle size. D_{50} represents the size of 50% of the

Table 1: Particle size of gypsum at a supersaturation ratio of 2.4 with and without cationic surfactants

Condition	D_{10} (μm)	D_{50} (μm)	D_{90} (μm)	D_{av} (μm)	$D[3,2]$ (μm)	$D[4,3]$ (μm)
Baseline	8.683	27.402	61.688	31.406	16.820	31.406
DDBAC 30 mg/L	8.474	30.662	70.574	35.646	16.891	35.046
DDBAC 50 mg/L	8.093	29.657	75.422	35.523	16.554	35.523
CMI 30 mg/L	8.741	28.494	60.461	31.684	17.332	31.684
CMI 50 mg/L	8.512	27.564	60.012	30.845	17.245	30.869

particles from the cumulative distribution. It means that the particles with a larger particle size account for 50%, and the smaller particles also account for 50% of the total number of particles. D_{50} is also known as the median diameter or the median particle size. Therefore, D_{50} is usually used to express particle size.

The D_{50} value increases by about 12% with the addition of 30 mg/L of DDBAC compared with the reference experiment at a supersaturation ratio of 2.4. However, the effect of increased particle size of gypsum diminishes with further increasing concentration of cationic surfactants. The D_{50} of gypsum increases with the addition of 30 mg/L of DDBAC by about 3.3% compared with the 50 mg/L at a supersaturation ratio of 2.4. The particle size of gypsum is higher in the presence of DDBAC compared to CMI.

The larger size of gypsum particles may indicate that the growth of the formed gypsum crystals is promoted compared to the reference, *i.e.*, the cationic surfactants promote the growth of gypsum.

3.2 Effect of cationic surfactants on the growth of gypsum

To further analyze the beneficial effect of the cationic surfactants on gypsum growth, the growth rate of gypsum under different working conditions was calculated.

The solution exhibits a linear relationship between the reaction time and the logarithm of the ion concentration (ln (*c*)), taking the supersaturation ratio of 2.4 as an example. The relationship between the reaction time and ln(*c*) at a supersaturation ratio of 2.4 with and without cationic surfactants is given in Figure 1 (similar to other supersaturation ratios). The fitting equations of the gypsum growth rate at a supersaturation ratio of 2.4 are given in Table 2. The R^2 of the fitting equations are all greater than 0.98, meaning that the fitting results are all very good. The equation can explain the change in experimental data very well, and the $K1$ calculated by the equation has high credibility.

The calculated gypsum growth rates at all investigated supersaturation ratios are given in Figure 2. These results reveal that the growth rate of gypsum increases with the addition of cationic surfactants. However, the effect of increased growth rate of gypsum diminishes with further increasing the concentration of cationic surfactants. With the addition of 30 mg/L of DDBAC, the growth rate of gypsum increases by about 50% compared with the reference experiment without surfactant at a supersaturation ratio of 2.4, and the growth rate of gypsum is higher in the presence of DDBAC compared to CMI. The presence of surfactants reduces the hydration status of calcium ions. Since the dehydration kinetics determines the gypsum crystal growth rate [5]. In addition, the adsorption of cationic

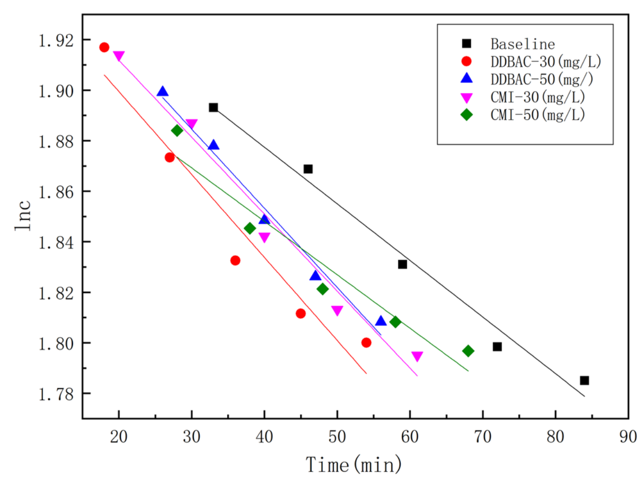

Figure 1: Relationship between time and ln(*c*) with and without cationic surfactants at a supersaturation ratio of 2.4.

Table 2: Fitting equations of the growth rate of gypsum at a supersaturation ratio of 2.4

Condition	Equation	R^2
Baseline	$y = -0.0022x + 1.967$	0.9845
DDBAC 30 mg/L	$y = -0.0033x + 1.9699$	0.9847
DDBAC 50 mg/L	$y = -0.0031x + 1.9786$	0.984
CMI 30 mg/L	$y = -0.003x + 1.9722$	0.98
CMI 50 mg/L	$y = -0.0023x + 1.9511$	0.9834

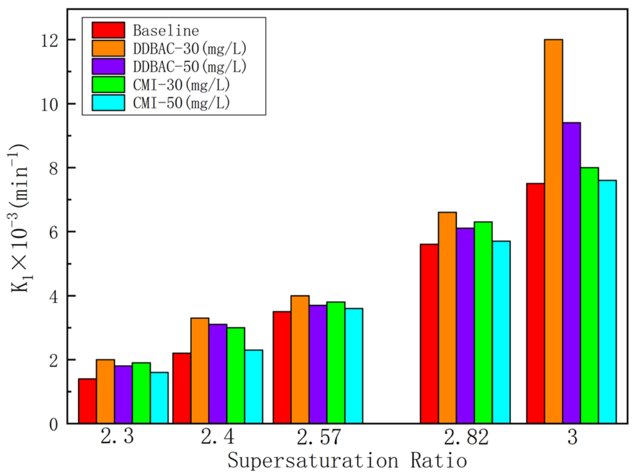

Figure 2: The results of calculation of the growth rate of gypsum at the studied supersaturation ratios with and without cationic surfactants.

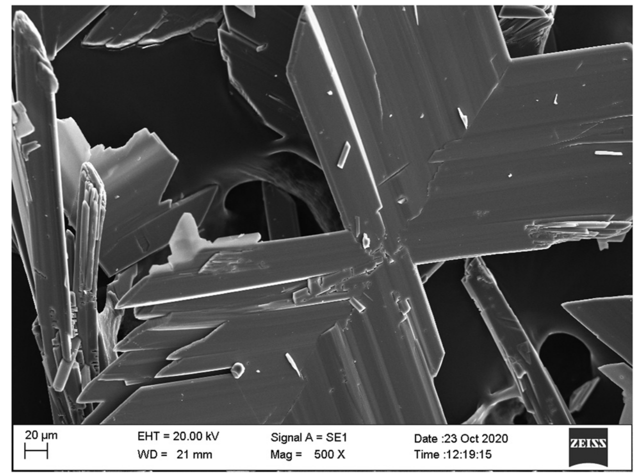

Figure 4: The morphology of gypsum with 30 mg/L DDBAC at a supersaturation ratio of 2.3.

surfactants on gypsum crystals leads to the decrease in crystal surface energy, which reduces the energy threshold for growth and promotes the crystallization of gypsum crystals. This can be seen in Table 1 and Figure 2. The growth rate of gypsum increases with its particle size. The higher the growth rate of gypsum is, the easier it is to grow into large crystals, which is beneficial to the dehydration of gypsum.

3.3 Effect of cationic surfactants on the gypsum morphology

One of the most important factors affecting gypsum dehydration is the morphology of gypsum crystals (size and shape of crystals); large crystals are desirable for optimal dehydration. The morphology of gypsum crystals in the absence of additives is given in Figure 3, indicating that the crystals exhibit a needle-like shape. The results of the gypsum morphology in the presence of DDBAC at concentrations of 30 and 50 mg/L at a supersaturation ratio of 2.3 are given in Figures 4 and 5, respectively. The majority of these crystals are tabular crystals. The morphology of gypsum crystals in the presence of CMI at concentrations of 30 and 50 mg/L at a supersaturation ratio of 2.3 are given in Figures 6 and 7, respectively. The majority of these crystals are also tabular crystals, which means that relatively thicker and larger crystals are formed. Plate-shaped crystals are more prone to dehydration than needle-shaped ones. The cationic surfactants facilitate the dehydration

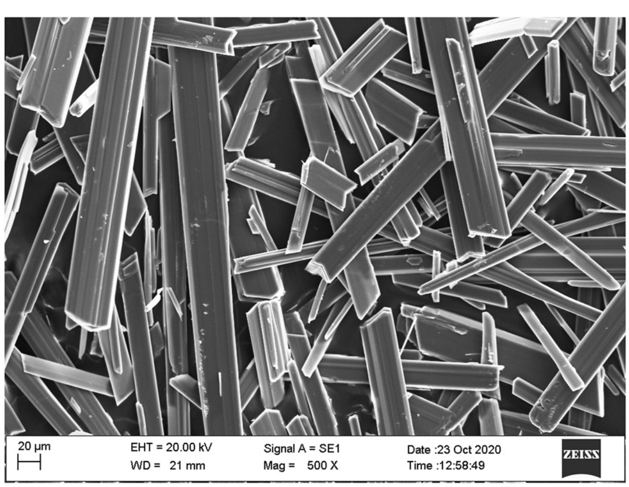

Figure 3: The morphology of gypsum without cationic surfactants at a supersaturation ratio of 2.3.

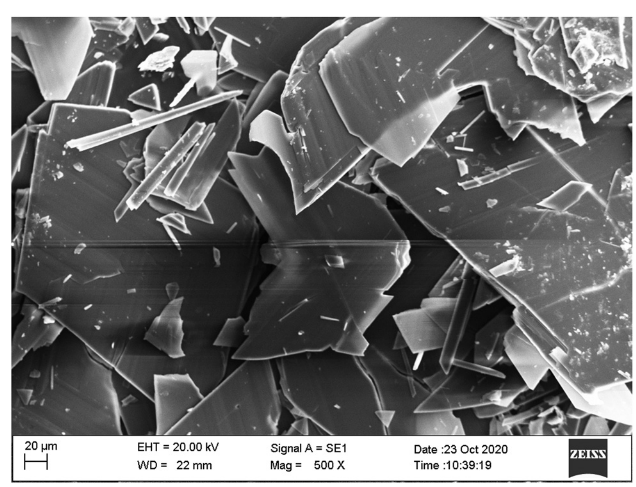

Figure 5: The morphology of gypsum with 50 mg/L DDBAC at a supersaturation ratio of 2.3.

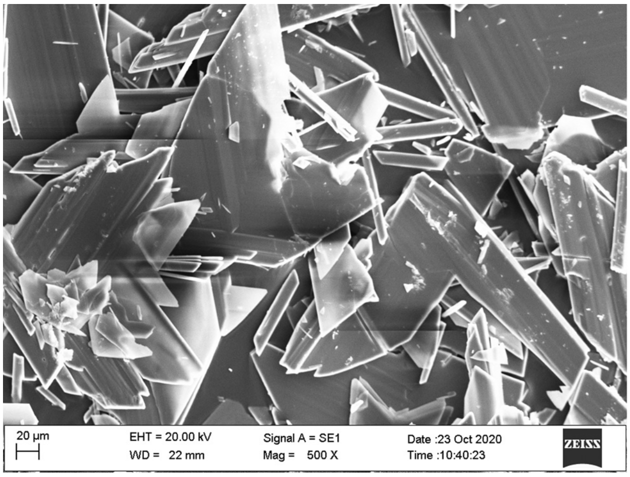

Figure 6: The morphology of gypsum with 30 mg/L CMI at a supersaturation ratio of 2.3.

of gypsum. Twin crystals are observed in Figures 4 and 5. The reason is that the additives in the solution lead to the formation of heterogeneous nuclei, which further grow into twin crystals [13–18]. On some of the SEM pictures, it can be seen that the crystals are broken, probably due to the relatively high agitation speed which causes more often collision of the forming particles with each other and the stirring rod. Twins and broken crystals are not conducive to gypsum dehydration. The formation of gypsum twins was inhibited by controlling solution concentration, reaction temperature, and adding nucleating agent. Adjust the stirring speed to avoid excessive stirring speed leading to a large number of fine broken crystals, affecting gypsum dehydration.

The average length-to-width ratio (L/W) of 50 crystals is 13.48:1 without additives, 6.21:1 with 30 mg/L DDBAC, 6.74:1 with 50 mg/L DDBAC, 7.12:1 with 30 mg/L CMI, and 7.81:1 with 50 mg/L CMI. The smaller L/W with DDBAC and CMI indicates the formation of thicker and larger crystals, which are favorable for gypsum dehydration.

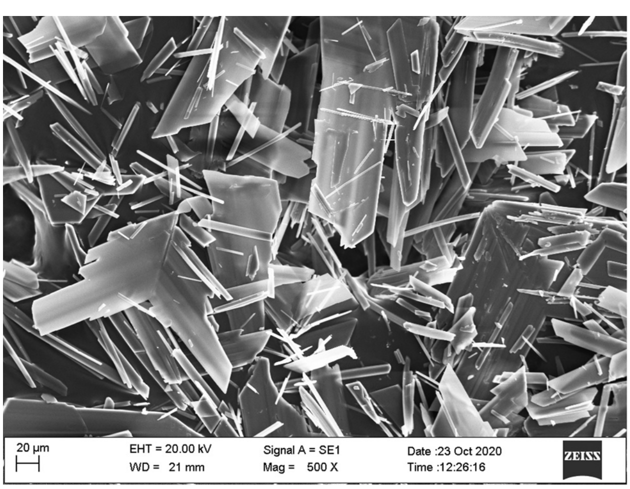

Figure 7: The morphology of gypsum with 50 mg/L CMI at a supersaturation ratio of 2.3.

Under the condition of desulfurization in coal-fired power plants, DDBAC and CMI can promote the growth of gypsum, transform the shape of gypsum into plate crystal, and reduce the ratio of length to diameter of gypsum crystal, which is beneficial to gypsum dehydration. DDBAC and CMI are conducive to the normal operation of the desulfurization and dehydration device, and they ensure the normal operation of the desulfurization process.

4 Conclusion

The effect of DDBAC and CMI on the calcium sulfate dihydrate growth under simulated conditions of desulfurization gypsum production was studied. Conductivity measurements were utilized to measure the growth rate, and the effects of DDBAC and CMI on the gypsum growth were further analyzed. The obtained results indicated several important findings:

The growth rate of gypsum increases in the presence of cationic surfactants. The growth rate is increased with the addition of 30 mg/L DDBAC by about 42.8% compared with the reference experiment at a supersaturation ratio of 2.4. The growth of gypsum is facilitated in the presence of DDBAC and CMI. The DDBAC exhibits a stronger effect than CMI on the gypsum growth. The effect of DDBAC and CMI on promoting gypsum growth decreases with further increase in the concentration of cationic surfactants.

Gypsum transforms from needle-like crystals to tabular crystals under the action of cationic surfactants. The average length-to-width ratio (L/W) decreases with the addition of DDBAC and CMI compared with the reference experiment without additives, which means that relatively thicker and larger crystals are formed.

Finally, DDBAC and CMI can promote the growth of gypsum, transform the morphology of gypsum into tabular crystal, and reduce the aspect ratio of gypsum crystal, which is beneficial to gypsum dehydration. The investigated cationic surfactants are beneficial to the normal operation of desulfurization systems in coal-fired power plants.

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