

# Kinetics Study on the Effect of NaCl on the CaSO<sub>4</sub> Dissolution Behavior

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**Abstract.** The study of the dissolution kinetics of CaSO<sub>4</sub> is essential for the control of the dissolution and recrystallization behavior of CaSO<sub>4</sub>. In this work, the kinetic behavior of CaSO<sub>4</sub> dissolved in NaCl solution was investigated by means of conductivity meter. The results show that with the increase of concentration of NaCl, the temperature rise and the time prolonged, the dissolution rate of dihydrate CaSO<sub>4</sub> gradually increases, and the dissolved apparent activation energy is gradually decreased. When the NaCl concentration is 1.8%, the dissolution kinetic equation is  $1-(1-\alpha)^{1/3}=5.46 \times 10^{-4} \exp(-9147/RT) t$ ; When the NaCl concentration is 3.0%, the dissolution kinetic equation is  $1-(1-\alpha)^{1/3}=2.81 \times 10^{-4} \exp(-6753/RT) t$ ; When the NaCl concentration is 3.6%, the dissolution kinetic equation is  $1-(1-\alpha)^{1/3}=3.07 \times 10^{-4} \exp(-6103/RT) t$ .

**Keywords:** CaSO<sub>4</sub>; NaCl, Dissolve; Dynamics

## 1. Introduction

With the increase in environmental awareness, the state has gradually increased the supervision of the enterprise environment, so the control technology of flue gas desulfurization has attracted much attention [1, 2]. At present, the flue gas desulfurization process mainly has lime-gypsum process, ammonia method and seawater desulfurization so on. In the process of flue gas desulfurization, not only the SO<sub>4</sub> adsorption and oxidation process, and the existence of CaSO<sub>4</sub> dissolved and mass transfer behavior [3, 4]. At present, there are few studies on the dissolution kinetics of CaSO<sub>4</sub>. Freyer studied the curves of different scholars on the solubility of CaSO<sub>4</sub> varies with NaCl concentration. It is shows that the concentration of NaCl in a certain range continues to increase, the solubility of CaSO<sub>4</sub> is also significantly increased, is the so-called "salt effect". Lancia et al [6]. Lancia et al. Through the measurement of the induction period found that when the relative supersaturation was 1 to 4 and the temperature was 25°C to 90°C, there is a significant nucleation activation energy (30kJ mol<sup>-1</sup>) and interfacial tension (37mJ m<sup>-2</sup>) in the CaSO<sub>4</sub> supersaturated solution; Jeschke [7] and Christoffersen [8] found that the dissolution rate of CaSO<sub>4</sub> solution decreases with increasing saturation, and the rate determining step gradually changes from the surface reaction-control to the diffusion control with increasing concentration. It is precisely because the dissolution behavior of CaSO<sub>4</sub> in solution not only affects the recovery of tail liquid after wet desulfurization, but more importantly, it is easy to cause pipeline and the container surface scaling, and thus cause the phenomenon of pipe clogging. Therefore, it is important to study the dissolution kinetics of CaSO<sub>4</sub>. In this paper, the iron concentration in the



solution was measured by means of a conductivity meter, study the dissolution kinetics of  $\text{CaSO}_4$  in NaCl solution, and provide a theoretical reference for the control of  $\text{CaSO}_4$  dissolution behavior.

## 2. Experimental Method

### 2.1. Experimental Materials and Equipment

Experimental materials for the chemical pure reagent dihydrate  $\text{CaSO}_4$  and NaCl. Equipment: conductivity meter, constant temperature bath and electronic balance.

### 2.2. Experiment Procedure

(1) The relationship between calibration of calcium ion concentration and conductivity. The slurry having a solid-liquid ratio of 1:10 was sufficiently stirred under different temperature conditions. And then filtered 250ml solution under constant temperature conditions, and the preparation of several different concentrations of  $\text{CaSO}_4$  solution. The solubility and corresponding conductivity values of  $\text{CaSO}_4$  were determined according to the national standard EDTA titration (GB-1892/2007). And then calculate the correspondence between the conductivity of the solution monitored on-line and the calcium concentration in the measured solution.

(2) Solution preparing. Poured 150ml of deionized water into the reaction vessel, according to the experimental scheme to add quantitative NaCl, then put the container in a constant temperature bath and heat it to the experiment set temperature, and then inserted into the electrode, record the conductivity value. Experimental conditions: The reaction temperatures were 25°C, 45°C, 65°C and 85°C, the solid-liquid proportional coefficient of dehydrate  $\text{CaSO}_4$  and water was 1:10, and the addition of NaCl was 1.8%, 3.0%, 3.6%, respectively. The stirring rate was controlled at 150rpm. Determination of the dissolution rate of dihydrate  $\text{CaSO}_4$ . At constant temperature, dihydrate  $\text{CaSO}_4$  was added to the reaction vessel, it was dried in the oven at 90°C for 4h in advance. And the curve of the conductivity value changes with time was recorded online in the solution, and then the calcium ion concentration in the solution is calculated by the fitted value.

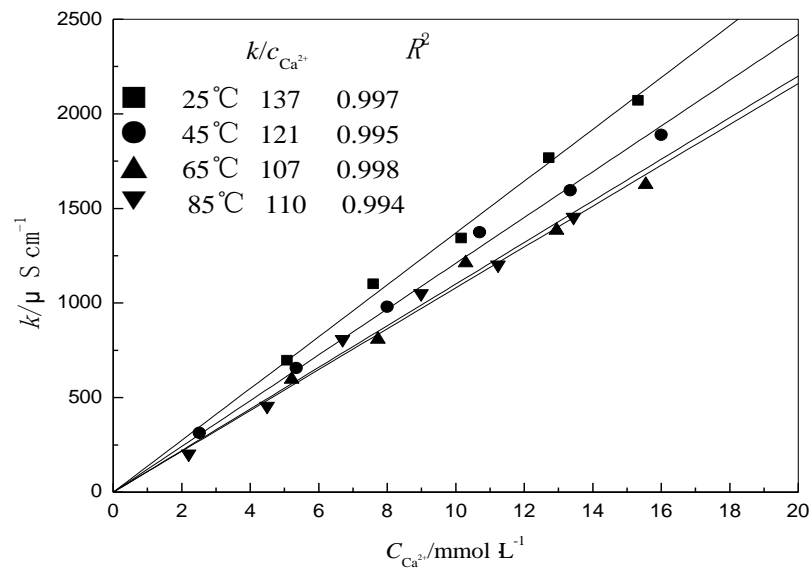
## 3. Results and Discussion

### 3.1. Determination of the Relationship between Calcium Ion Concentration and Conductivity in Solution

The concentration of  $\text{Ca}^{2+}$  in the solution was 15.23 mmol L<sup>-1</sup>, 15.93 mmol L<sup>-1</sup>, 15.45 mmol L<sup>-1</sup> and 13.81 mmol L<sup>-1</sup> by EDTA method at 25°C, 45°C, 65°C and 85°C. And then the saturated solution at each temperature isothermal dilution of a certain proportion to obtain a number of different  $C_{\text{Ca}^{2+}}$  calibration solution, and then measured the conductivity  $k$  of the calibration solution, and the corresponding values of  $C_{\text{Ca}^{2+}}$  and  $k$  were obtained respectively. As shown in Figure 1, the slope is the proportional coefficient of the conductivity  $k$  to the calcium ion concentration  $C_{\text{Ca}^{2+}}$  at this temperature, the results are basically consistent with the literature [9]. The proportional coefficient of the different temperature is not the same, but the correlation coefficient remained at 0.988~0.977, the linearity was very good, which indicated that it was feasible to determine the calcium ion concentration  $C_{\text{Ca}^{2+}}$  in the solution by the conductivity method. Therefore, the concentration of calcium ions in the solution can be measured with the conductivity measurement.

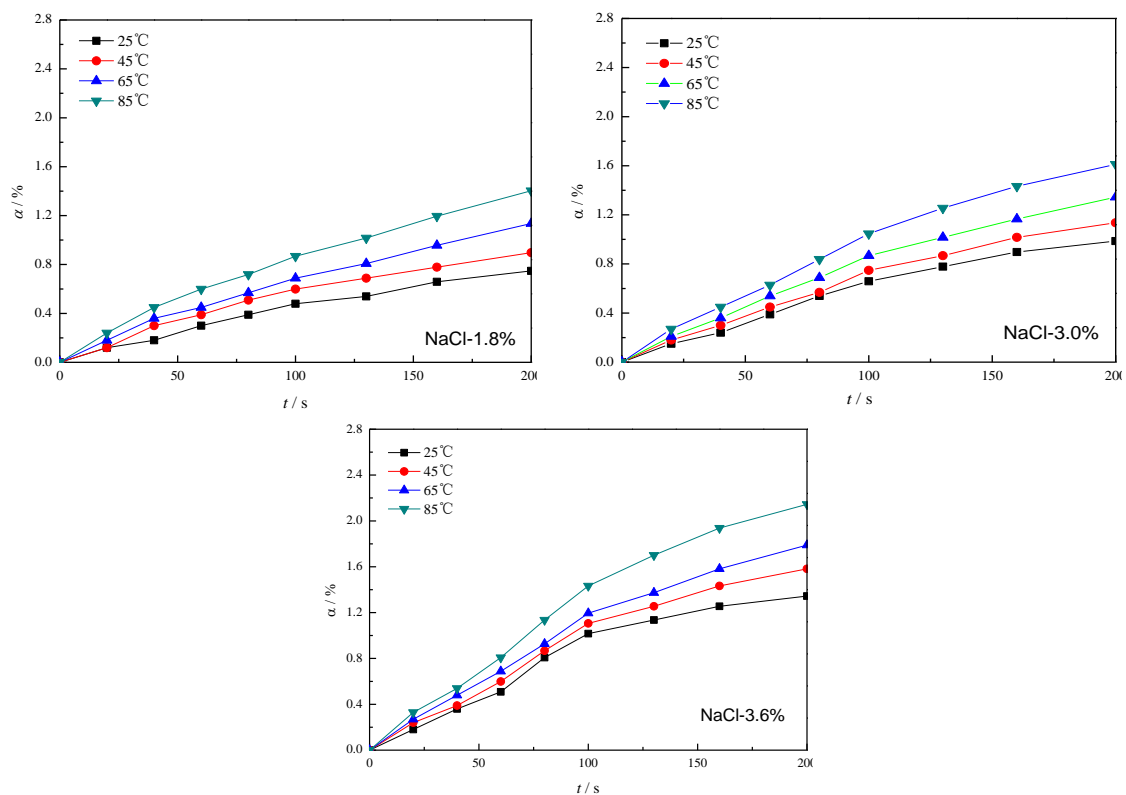
### 3.2. Effect of NaCl Concentration on Dissolution Behavior of $\text{CaSO}_4$

Figure 2 shows the curve of the change in the dissolution rate  $\alpha$  of dihydrate  $\text{CaSO}_4$  over time with different NaCl additions. The dissolution rate  $\alpha$  is the ratio of the total amount of calcium ions in the solution to the total amount of calcium in the added dihydrate  $\text{CaSO}_4$ . It can be seen from the figure, with the dissolution time and temperature rise, the dissolution rate and dissolution rate of dihydrate  $\text{CaSO}_4$  has increased. This phenomenon is related to the molecular thermodynamic movement, the temperature increases, the molecular thermodynamic movement of solid is accelerated, so that the dissolution rate of solid  $\text{CaSO}_4$  becomes faster.



**Figure 1.** Relationships between  $CCa^{2+}$  and conductivity  $K$  under different temperature

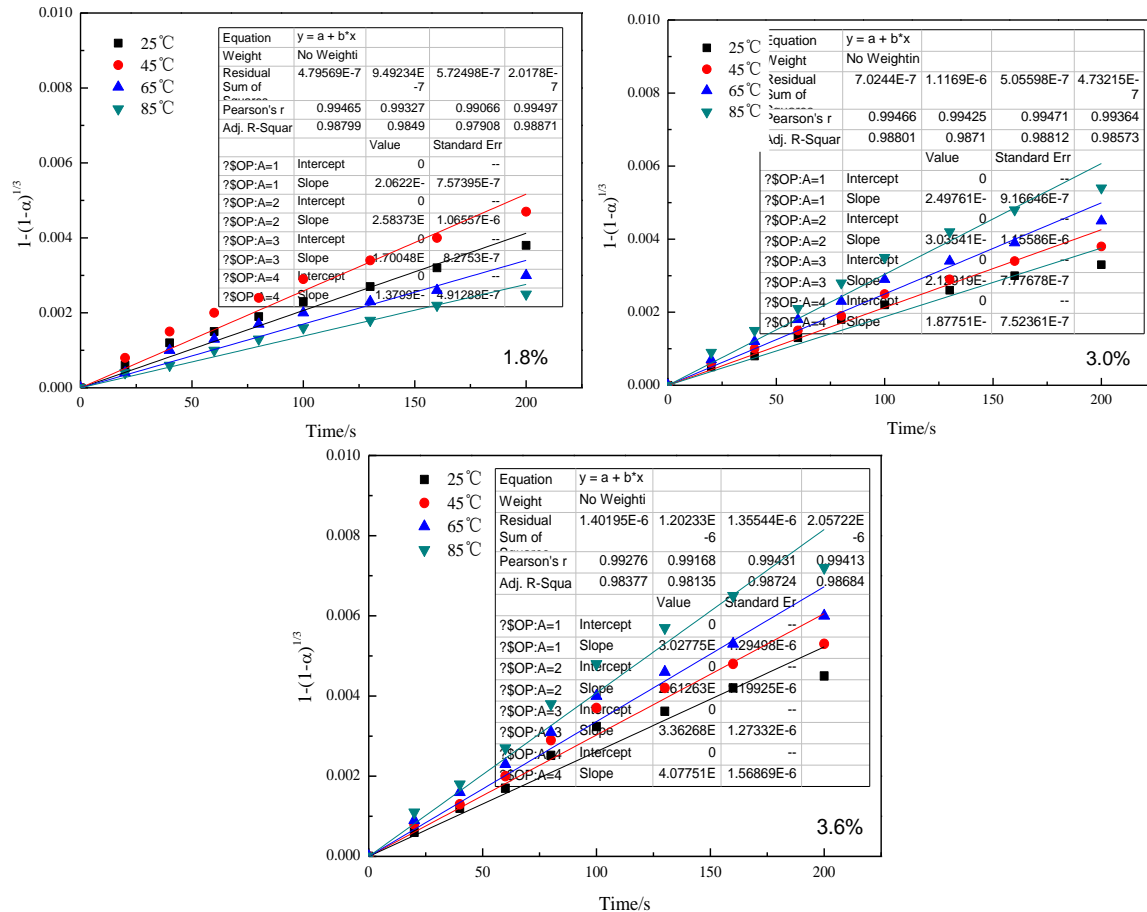
In general, for the liquid-solid two-phase shrinkage kinetics model, the two equations of  $1-(1-\alpha)^{1/3}=Kt$  and  $1-1/3(1-\alpha)^{2/3}=Kt$  are used to linear fit, where  $K$  is the rate of dissolution reaction rate constant ( $s^{-1}$ ),  $\alpha$  is the dissolution rate (%), and  $t$  is the time (s).



**Figure 2.** The dissolving rate under different NaCl content, temperature and time change curve

When there is NaCl in the solution, there is no product layer on the surface during the dissolution of  $CaSO_4 \cdot 2H_2O$ , and the diffusion resistance can be eliminated under the action of higher stirring

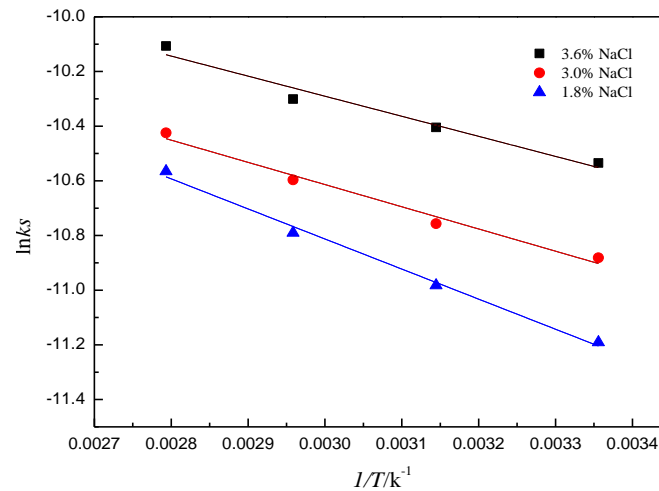
speed. At this time,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  dissolving process is only controlled by equilibrium dissolution. Figure 2 in accordance with the commonly used equation fitting, as shown in Figure 3. The correlation of  $1-(1-\alpha)^{1/3}=Kt$  was higher, and the  $R$  value was higher than 0.98 or more.



**Figure 3.** Line relationship between time and the mechanism of  $1-(1-\alpha)^{1/3}$  of linear under different temperature

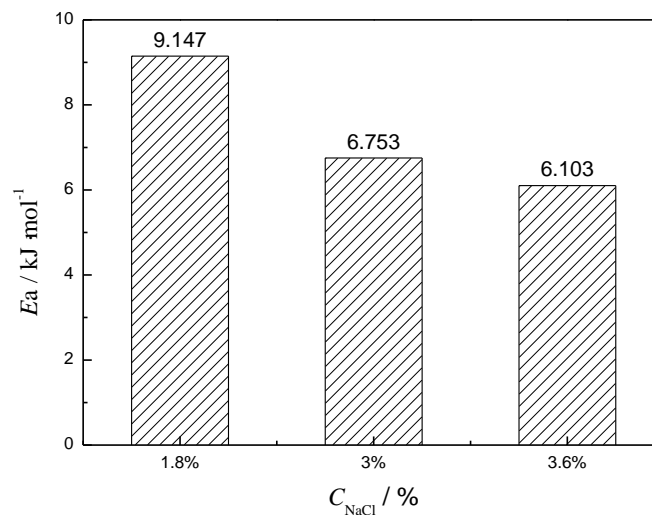
Using Arrhenius equation by  $\ln K$  and  $1/T$  mapping, as shown in Figure 4. It can be seen from the figure, the linear correlation of 0.96 or more, by fitting the linear slope obtained  $-E/R$ , interception for the  $\ln A$ ,  $E$  and  $A$  can be obtained.

Figure 5 shows the apparent activation energy of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  dissolved under different NaCl concentrations. It can be seen that with the increase of NaCl concentration, according to the Debye-Huckel theory, NaCl can reduce the activity coefficient of  $\text{CaSO}_4$  solution, increase the activity of  $\text{CaSO}_4$ , increase the activation center and increase the effective collision, which is beneficial to the interaction between ions, which leads to the decrease of apparent activation energy of  $\text{CaSO}_4$  dissolution.



**Figure 4.** Corresponding relations between  $\ln k_s$  versus  $1/T$

The dissolution kinetics equation of dihydrate  $\text{CaSO}_4$  in different NaCl concentration solution can be obtained by using activation energy  $K=A \times \exp(-E/RT)$ , where  $k$  is the reaction rate constant;  $E$  is the apparent dissolution activation energy of dihydrate  $\text{CaSO}_4$ ;  $A$  is the frequency factor;  $R$  is the ideal gas constant;  $T$  is the solution temperature. The kinetic equation of dissolution of dihydrate  $\text{CaSO}_4$  under the condition of NaCl 1.8% concentration is:  $1-(1-\alpha)^{1/3}=5.46 \times 10^{-4} \exp(-9147/RT)t$ ; The kinetic equation of dissolution of dihydrate  $\text{CaSO}_4$  under the condition of NaCl 3.0% concentration is:  $1-(1-\alpha)^{1/3}=2.81 \times 10^{-4} \exp(-6753/RT)t$ ; The kinetic equation of dissolution of dihydrate  $\text{CaSO}_4$  under the condition of NaCl 3.6% concentration is:  $1-(1-\alpha)^{1/3}=3.07 \times 10^{-4} \exp(-6103/RT)t$ . With the increase of NaCl concentration, the dissolution rate of dihydrate  $\text{CaSO}_4$  gradually increased.



**Figure 5.** The relationship between the amount of activation energy and NaCl

#### 4. Conclusions

Under the experimental condition, with the increase of NaCl concentration, the temperature rise and the time prolonged, the dissolution rate of dihydrate  $\text{CaSO}_4$  gradually increased, and the apparent activation energy of dissolution gradually decreased. The dissolution kinetics of dihydrate  $\text{CaSO}_4$  in aqueous NaCl solution is as follows: The kinetic equation for NaCl concentration of 1.8% is

$1-(1-\alpha)^{1/3}=5.46 \times 10^{-4} \exp(-9147/RT)t$ ; The kinetic equation for NaCl concentration of 3.0% is  $1-(1-\alpha)^{1/3}=2.81 \times 10^{-4} \exp(-6753/RT)t$ ; The kinetic equation for NaCl concentration of 3.6% is  $1-(1-\alpha)^{1/3}=3.07 \times 10^{-4} \exp(-6103/RT)t$ .

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