

# Thermodynamic Stability and Dissolution of Calcium Fluoride of Phosphogypsum Solidified in Cement-Based Cementing Materials in Bicarbonate Solution

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Cement-based cementitious materials present an alkaline environment and mainly exist in the form of  $\text{Ca}(\text{OH})_2$ . Phosphogypsum, as a retarder of cementitious materials, is often added to cement instead of gypsum, and the fluorine by-product of phosphogypsum is also fixed in the form of  $\text{CaF}_2$ . These cement-based materials often serve in environments containing carbonate groundwater, which changes the stability of solidified  $\text{CaF}_2$ . This paper studied the solid and liquid changes in  $\text{Ca}(\text{OH})_2\text{-CaF}_2$ ,  $\text{Ca}(\text{OH})_2\text{-CaF}_2\text{-HCO}_3^-$ ,  $\text{CaF}_2\text{-HCO}_3^-\text{-OH}$  systems, and therefore studied the solubility of the by-product  $\text{CaF}_2$  of phosphogypsum in the groundwater containing  $\text{HCO}_3^-$  anion after curing in the cement-based cementitious system through experiments and thermodynamic equation simulation. The results showed that the dissolved  $\text{Ca}^{2+}$  of  $\text{Ca}(\text{OH})_2$  led to the dissolution of  $\text{CaF}_2$ , which led to a significant reduction in the  $\text{F}^-$  anion concentration. However, with the increase of  $\text{HCO}_3^-$  concentration in groundwater, the  $\text{F}^-$  anion concentration of  $\text{Ca}(\text{OH})_2\text{-CaF}_2\text{-HCO}_3^-$  system increased, and the main product formed in the solid phase was calcium carbonate; The dissolution of  $\text{F}^-$  anions in  $\text{CaF}_2\text{-HCO}_3^-\text{-OH}$  system also increased with the increase of  $\text{HCO}_3^-$  concentration. Therefore, the influence of  $\text{HCO}_3^-$  in groundwater should be considered when using phosphogypsum instead of gypsum as a retarder in cement-based cementitious materials.

**Keywords:** fluorine anion, bicarbonate, Raman spectrum, thermodynamic equilibrium.

## 1. INTRODUCTION

Phosphogypsum is a solid waste produced in the wet-process phosphoric acid process of the phosphorous chemical industry. The main component of phosphogypsum is  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and its mass fraction can reach 75 % ~ 95 %, but it also contains a small amount of sulfuric acid and phosphoric acid, so that phosphogypsum shows acidity and the pH value is between 1.5 and 5.5 [1]. Due to the different sources of phosphate rock, phosphogypsum produced in various places contains different amounts of fluorine anions. Fluoride anion is a kind of toxic ion, and Fluorosis can cause damage to teeth, bones, and even the brain [2, 3]. Phosphogypsum around the storage yard can cause heavy metals to exceed the standard concentration seriously, and the distribution of heavy metals in different areas is uneven [4]. The release of harmful impurities such as residual fluoride, free phosphoric acid and some heavy metals also affect people's health [5]. Moreover, phosphogypsum in some areas also has radioactive hazards [6]. Therefore, free  $\text{P}_2\text{O}_5$ ,  $\text{F}^-$  and some heavy metals in phosphogypsum need to be treated innocuously during its regeneration and utilization.

Currently, the commonly used impurity removal methods for comprehensive utilization of phosphogypsum can be divided into three categories: physical method, chemical method, and physical chemical heat treatment method [1]. Jinming Wang et al. removed soluble phosphorus and fluorine by adding lime, and purified phosphogypsum by flotation, increasing the whiteness of phosphogypsum from 31.5 to 58.4. The percentage of total phosphorus ( $\text{P}_2\text{O}_5$ ) in gypsum was reduced from 1.78 to

0.89, and the grade of calcium sulfate dihydrate was 96.6 % [7]. Chen Qianhao et al. found that the pH value of phosphogypsum and the liquid-solid ratio of the pre-treatment solution were in a quadratic function increasing relationship, so increasing the pH value of phosphogypsum through pre-treatment can produce a coagulation-promoting effect [8]. Fornés et al. pointed out that if  $\text{Ca}(\text{OH})_2$  admixture was added, impurities such as soluble  $\text{F}^-$  and  $\text{P}_2\text{O}_5$  can be neutralized [9]. S. Liu found that the minimum requirement for  $\text{Ca}(\text{OH})_2$  was only 2 % [10]. Gijbels K et al. mixed the mortar with phosphogypsum from different sources in different proportions, and found that the fixation ratio of mixed mortar to  $\text{F}^-$  exceeded 99 %. However, the author also pointed out that it was necessary to be cautious when extrapolating the laboratory leaching test to the long-term service process [11]. Wang Zhijuan et al. showed that  $\beta$ -phosphogypsum and citric acid can improve the performance of mortar [12].

Because phosphogypsum contains a large amount of gypsum which has a retarding effect on Portland cement, it can be used as a retarder for cement concrete. José S. Andrade Neto et al. showed that phosphogypsum can be used as the retarder of Portland cement. However, the water soluble  $\text{P}_2\text{O}_5$  and  $\text{F}^-$  in the untreated phosphogypsum delayed the hydration of cement and led to the strength reduction of cement mortar [13]. Ana Rita Damasceno Costa et al. studied the role of phosphogypsum in the ternary system containing Portland cement, marble and clay brick waste, and found that the retarding effect of phosphogypsum was mainly to prolong the induction period of cement hydration process [14]. Zhao Fengwen et al. used cement and lime to excite some oxides in phosphogypsum, which

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can produce a small amount of pozzolanic reaction, and also react with residual acid in phosphogypsum to eliminate the acidity of phosphogypsum [15]. Xu Fang et al. studied the preparation of phosphogypsum slag cement by activating slag powder with phosphogypsum adding a small amount of cement or clinker, and found that more ettringite which can promote strength can be produced in the alkaline environment [16]. S. Andrade Neto et al. found that chemical treatments based on  $\text{Ca}(\text{OH})_2$  reduced the concentration of impurities in phosphogypsum (water soluble phosphorus decreased by 80.3 %) [13]. At present, some cement production enterprises also use this mechanism for pretreatment. Before phosphogypsum was added to cement clinker, lime was added for pretreatment, so that the soluble ions in phosphogypsum can be converted into  $\text{Ca}_3(\text{PO}_3)_2$  and  $\text{CaF}_2$ , etc.

However, the service time of cement-based cementitious materials was very long, and the consequences of phosphogypsum in the service process can be more serious. The environmental and human health risks caused by the long-term impact of these pollutants on human beings should be considered [17]. As  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  in phosphogypsum was consumed as a retarder in cement-based materials to form ettringite, the most other ions were mainly fluorine anions, forming  $\text{CaF}_2$  in cement-based materials. Cement-based materials can encounter the impact of groundwater during service, especially the erosion of flowing water. During the investigation of groundwater,  $\text{HCO}_3^-$  anion was a common anion found in groundwater [18]. It can precipitate with  $\text{Ca}^{2+}$  ion, which may promote the dissolution of solidified  $\text{CaF}_2$  in phosphogypsum, thus making the solidified fluoride anions had risk of leaching.

Cement-based materials were alkaline materials in which the alkaline substance was mainly  $\text{Ca}(\text{OH})_2$ . When cement-based materials encountered groundwater containing  $\text{HCO}_3^-$  anion,  $\text{Ca}(\text{OH})_2$  in cement-based materials formed a complex chemical system with phosphogypsum and  $\text{HCO}_3^-$  in groundwater, which constituted the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$  system. When the  $\text{Ca}^{2+}$  ions in the  $\text{Ca}(\text{OH})_2$  were depleted,  $\text{Ca}(\text{OH})_2$  was converted to  $\text{OH}^-$ , resulting in the formation of a  $\text{CaF}_2$ - $\text{HCO}_3^-$ - $\text{OH}$  system. Therefore,  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$  and  $\text{CaF}_2$ - $\text{HCO}_3^-$ - $\text{OH}$  systems were used to study the stability of  $\text{CaF}_2$  internally solidified during the early and late dissolution processes of cement-based materials under the influence of  $\text{HCO}_3^-$  in external groundwater. The study of this method was beneficial for reducing experimental errors caused by the dissolution of other small amounts of ions in cement-based materials and simplifying the chemical reaction process in this process.

## 2. MATERIALS AND METHODS

### 2.1. Materials

#### 2.1.1. Raw materials

To simulate the dissolution process of cement-based materials, the most important dissolved part  $\text{Ca}(\text{OH})_2$  (Damao chemical reagent plant, AR) was used for simulation research; The solidified fluoride ions were directly studied using the chemical reagent  $\text{CaF}_2$  (Sinopharm Chemical ReagentCo., Ltd, AR); The study of

bicarbonate ions in groundwater using the chemical reagent  $\text{NaHCO}_3$  (Sinopharm Chemical ReagentCo., Ltd, AR); The alkaline environment of the system is regulated using  $\text{NaOH}$  (Sinopharm Chemical ReagentCo., Ltd, AR); Distilled water.

#### 2.1.2. Proportion of mixture

In the early stage,  $\text{Ca}(\text{OH})_2$  was mainly dissolved in cement-based materials, and the solidified  $\text{CaF}_2$  and  $\text{HCO}_3^-$  in groundwater jointly formed the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$  system; When the  $\text{Ca}^{2+}$  ions are consumed, the  $\text{CaF}_2$ - $\text{HCO}_3^-$ - $\text{OH}$  system was then formed. Therefore, these two systems had been designed, and their design proportions were shown in Table 1.

**Table 1.** Proportion of mixture of systems

System	$\text{CaF}_2$ , g	$\text{NaOH}$ , g	$\text{Ca}(\text{OH})_2$ , g	$\text{NaHCO}_3$ , g	Water, mL
$\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$	2.5	0	2.5	5.04	150
	2.5	0	2.5	10.08	150
	2.5	0	2.5	15.12	150
$\text{CaF}_2$ - $\text{HCO}_3^-$ - $\text{OH}$	2.5	0.080	0	0.177	150
	2.5	0.080	0	0.856	150
	2.5	0.080	0	1.687	150
	2.5	0.080	0	5.059	150
	2.5	0.080	0	8.523	150

## 2.2. Experimental methods

### 2.2.1. Detection of concentration of $\text{F}^-$ in $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$ and $\text{CaF}_2$ - $\text{HCO}_3^-$ - $\text{OH}$ systems

By mixing and stirring  $\text{Ca}(\text{OH})_2$ ,  $\text{CaF}_2$ ,  $\text{NaHCO}_3$ ,  $\text{NaOH}$  and water according to the proportion of mixture in Table 1, and after the ion concentration stabilized, the concentration of  $\text{F}^-$  in the cement-based material was detected using a fluoride ion analyzer to simulate the changes in dissolved ions during the dissolution stage.

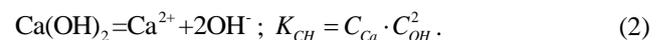
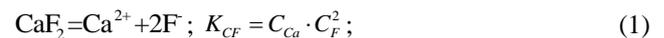
### 2.2.2. Component analysis in the system

Due to the low requirements of Raman spectroscopy on samples, it was used to characterize changes in substances in the solid phase. The solid state in the system was filtered and dried, and the material changes before and after the chemical reaction were detected by Raman spectroscopy.

## 3. RESULTS AND DISCUSSION

### 3.1. Calculation of critical concentration of $\text{CaF}_2$ , $\text{Ca}(\text{OH})_2$ and $\text{NaHCO}_3$

The critical concentrations of  $\text{CaF}_2$  and  $\text{Ca}(\text{OH})_2$  are stable, and the following equilibria exist in this process:

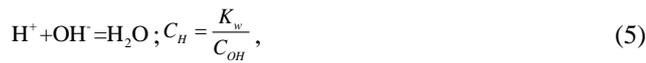
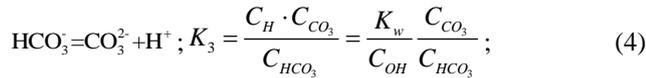
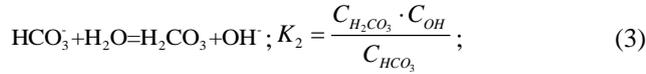


where  $K_{CF}$  and  $K_{CH}$  were the solubility product constants of  $\text{CaF}_2$  and  $\text{Ca}(\text{OH})_2$ , respectively;  $C_{Ca}$ ,  $C_F$  and  $C_{OH}$  were the concentration of  $\text{Ca}^{2+}$ ,  $\text{F}^-$  and  $\text{OH}^-$  respectively when the system reached chemical equilibrium.

Thermodynamic equilibrium constants of reactions were from Ref. [19], After calculation, the  $\text{Ca}^{2+}$  ion

concentration of saturated  $\text{CaF}_2$  after equilibrium was 0.001098 mol/L, and  $\text{F}^-$  anion concentration was 0.002197 mol/L; and  $\text{Ca}^{2+}$  ions concentration of  $\text{Ca}(\text{OH})_2$  after equilibrium was 0.011 mol/L, and the  $\text{OH}^-$  anion concentration was 0.022 mol/L.

$\text{HCO}_3^-$  can react with  $\text{H}_2\text{O}$  chemically to form a hydrolysis reaction, and can also undergo electrolysis reaction:



where  $K_2$ ,  $K_3$  and  $K_w$  were the standard equilibrium constant of Eq. 3, Eq. 4 and Eq. 5, respectively;  $C_{\text{H}_2\text{CO}_3}$ ,  $C_{\text{HCO}_3^-}$ ,  $C_{\text{H}^+}$  and  $C_{\text{CO}_3^{2-}}$  were the concentration of  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$  respectively when the system reached chemical equilibrium.

It can be seen that  $\text{HCO}_3^-$  can lead to an increase in the concentration of  $\text{OH}^-$  in the solution through hydrolysis, that was, to an increase in the pH of the solution; however,  $\text{HCO}_3^-$  can form more  $\text{H}^+$  through ionization, which led to lower pH of the system; therefore, the pH of  $\text{HCO}_3^-$  solution was the result of hydrolysis and ionization. The relationship between the pH of the solution and the added  $\text{HCO}_3^-$  in the equilibrium state can be obtained by calculating Eq. 3–Eq. 5, and the result was shown in Eq. 6:

$$C_{\text{HCO}_3^-(T)} = \frac{[(C_{\text{OH}^-}]^2 - K_w)[K_3 \cdot (C_{\text{OH}^-}]^2 + K_2 K_w + K_w C_{\text{OH}^-}]}{K_2 K_w C_{\text{OH}^-} - K_3 (C_{\text{OH}^-}]^3}. \quad (6)$$

Among them,  $C_{\text{HCO}_3^-(T)}$  was the concentration of total  $\text{HCO}_3^-$  anions added to the system. The relationship between  $\text{HCO}_3^-$  and pH in Fig. 1 can be obtained by the calculation of Eq. 6.

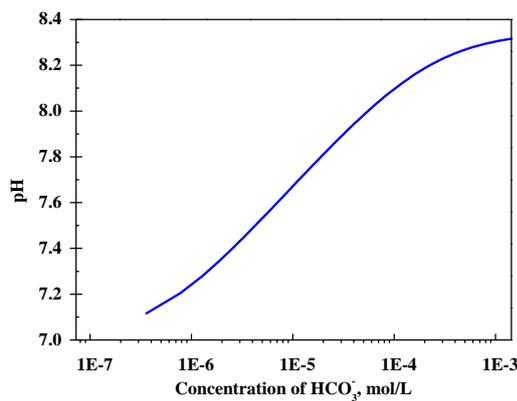


Fig. 1. pH in  $\text{HCO}_3^-$  solution

It can be seen that in  $\text{HCO}_3^-$  solution, the pH of the solution was not fixed, but increased with the increase of original  $\text{HCO}_3^-$ . The pH of the  $\text{HCO}_3^-$  solution was greater than 7, that was, the solution was slightly alkaline. Therefore, the reaction trend in  $\text{HCO}_3^-$  solution was that hydrolysis was greater than ionization.

### 3.2. Calculation of critical concentration of $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ system

If there was no disturbance of  $\text{HCO}_3^-$  in the system,  $\text{Ca}(\text{OH})_2$  and  $\text{CaF}_2$  as insoluble substances can not react with each other, and there was only solution-precipitation equilibrium between them.  $\text{CaF}_2$  exist in the solution-precipitation equilibrium of Eq. 1, and  $\text{Ca}(\text{OH})_2$  exist in the equilibrium of Eq. 2. In the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$  system, there were three kinds of ions:  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ , and the relationship was:

$$C_{\text{Ca}} = \frac{1}{2} C_{\text{OH}^-} + \frac{1}{2} C_{\text{F}^-}. \quad (7)$$

Combining Eq. 1 and Eq. 2, Eq. 7 can be solved. After calculation, the  $\text{Ca}^{2+}$  ion concentration of  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$  system after equilibrium was 0.0113 mol/L, while the  $\text{F}^-$  anion concentration was  $6.83 \times 10^{-4}$  mol/L,  $\text{OH}^-$  anion concentration was 0.022 mol/L (pH = 12.34). Therefore, it can be seen that under the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$  system,  $\text{Ca}^{2+}$  ion concentration and  $\text{OH}^-$  anion concentration in the system had little change, but the dissolved amount of  $\text{F}^-$  anion concentration in the system had decreased significantly. This was due to Le Chatelier's principle [20], the solubility of  $\text{Ca}(\text{OH})_2$  was large, and the dissolved  $\text{Ca}^{2+}$  ion concentration led to the dissolution of  $\text{CaF}_2$ , which led to a significant reduction in the  $\text{F}^-$  anion concentration.

### 3.3. Detection of Raman spectroscopy and critical concentration of $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$ system

After mixing  $\text{Ca}(\text{OH})_2$ ,  $\text{CaF}_2$  and  $\text{NaHCO}_3$  and fully stirring, the corresponding solid part was dried for Raman spectroscopy, and the results were shown in Fig. 2.

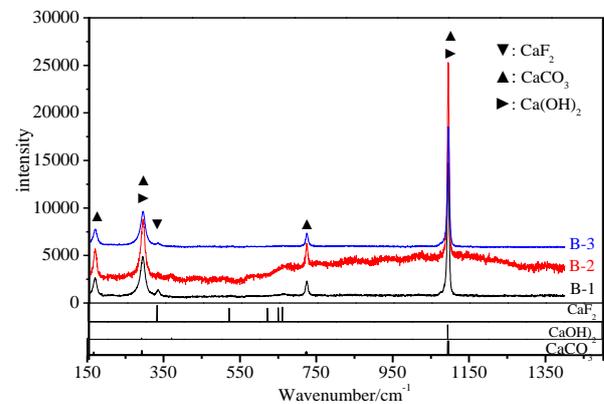
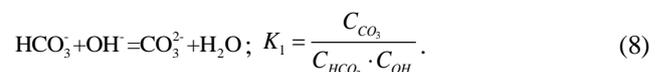


Fig. 2. Raman spectra in  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  solution

It can be seen from the Raman spectrum that the solid part mainly includes  $\text{CaF}_2$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , etc. Therefore, it can be seen that  $\text{Ca}(\text{OH})_2$  and  $\text{CaF}_2$  can undergo dissolution reaction in an aqueous solution, while under the disturbance of  $\text{HCO}_3^-$  in the system, there was not only the trend and solution-precipitation equilibrium as shown in Eq. 1–Eq. 2, but also the following chemical reactions in the process:

1.  $\text{HCO}_3^-$  can react with  $\text{OH}^-$  to form a neutralization reaction:



2. The formed  $\text{CO}_3^{2-}$  precipitated with the dissolved  $\text{Ca}^{2+}$  of  $\text{Ca}(\text{OH})_2$  and  $\text{CaF}_2$ :

$$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3; K_{CC} = C_{Ca} \cdot C_{\text{CO}_3} \quad (9)$$

where  $K_1$  was the standard equilibrium constant of Eq. 8, and  $K_{CC}$  was the solubility product constant of Eq. 9.

In the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  system, there were five ions such as  $\text{Ca}^{2+}$ ,  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  through dissolution and other processes. The existing relationship was:

1. Calcium equilibrium.

Calcium ions in the solution should be equal to the amount of  $\text{Ca}^{2+}$  dissolved in  $\text{Ca}(\text{OH})_2$  and  $\text{CaF}_2$  minus the amount of  $\text{Ca}^{2+}$  formed in  $\text{CaCO}_3$ , where the  $\text{Ca}^{2+}$  dissolved in  $\text{Ca}(\text{OH})_2$  can be equal to half of the dissolved  $\text{OH}^-$  anions, and the calcium ions dissolved in  $\text{CaF}_2$  can be equal to half of the dissolved  $\text{F}^-$  anions:

$$C_{Ca} = \frac{1}{2}C_{\text{OH}} + \frac{1}{2}C_{\text{CO}_3} + \frac{1}{2}C_F - \frac{1}{2}C_{\text{CaCO}_3}. \quad (10)$$

Among them,  $C_{\text{CaCO}_3}$  was the content of  $\text{CaCO}_3$ .

2. Carbon element equilibrium.

The amount of  $\text{HCO}_3^-$  anions in the solution ( $C_{\text{HCO}_3}$ ) should be equal to the total amount of  $\text{HCO}_3^-$  anions ( $C_{\text{HCO}_3(\text{T})}$ ) minus the amount of  $\text{CO}_3^{2-}$  anions minus the amount of  $\text{Ca}^{2+}$  formed by  $\text{CaCO}_3$ .

$$C_{\text{CaCO}_3} = C_{\text{HCO}_3(\text{T})} - C_{\text{CO}_3} - C_{\text{HCO}_3}. \quad (11)$$

Combining Eq. 1 and Eq. 2, Eq. 8 and Eq. 9 into Eq. 10 and Eq. 11 can be solved.

$$C_{\text{HCO}_3(\text{T})} = \frac{\left( \sqrt{K_{\text{CH}}} + \sqrt{K_{\text{CF}}} + \frac{K_{\text{CC}}}{K_1 \cdot \sqrt{K_{\text{CH}}}} \right)}{\sqrt{C_{Ca}}} + \frac{2K_{\text{CC}} - 2C_{Ca}}{C_{Ca}}. \quad (12)$$

After calculation, the changes and experimental results of various ions in the  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  system after equilibrium were as Fig. 3. The concentration of  $\text{F}^-$  anions measured by the 2.2.1. method was also listed in Fig. 3. Since the concentration of  $\text{F}^-$  anions in the system was small, it was expressed by the natural logarithm (pF) of ion concentration:

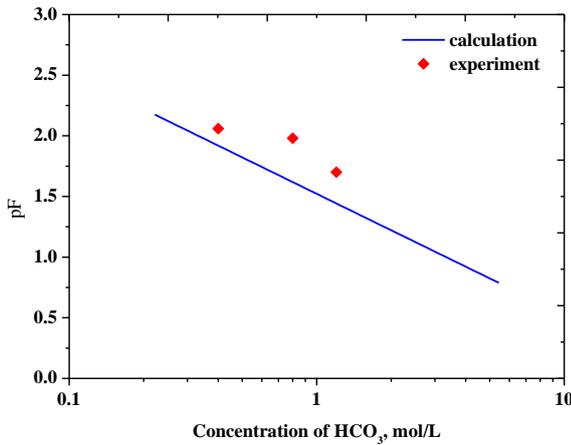


Fig. 3. pF in  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  system solution

It can be seen that the theoretical and practical results were in good agreement, that was, with the increase of  $\text{HCO}_3^-$  concentration, the value of pF gradually decreased,

that was, the dissolved  $\text{F}^-$  anion concentration gradually increased. Therefore,  $\text{HCO}_3^-$  in the solution can promote the dissolution of  $\text{F}^-$  anions in  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  system.

### 3.4. Detection of Raman spectroscopy and critical concentration of $\text{CaF}_2$ - $\text{HCO}_3$ - $\text{OH}$ system and $\text{CaF}_2$ - $\text{NaHCO}_3$ system

After mixing  $\text{NaOH}$ ,  $\text{CaF}_2$  and  $\text{NaHCO}_3$  and fully stirring, the corresponding solid part was dried for Raman spectroscopy, and the results were shown in Fig. 4.

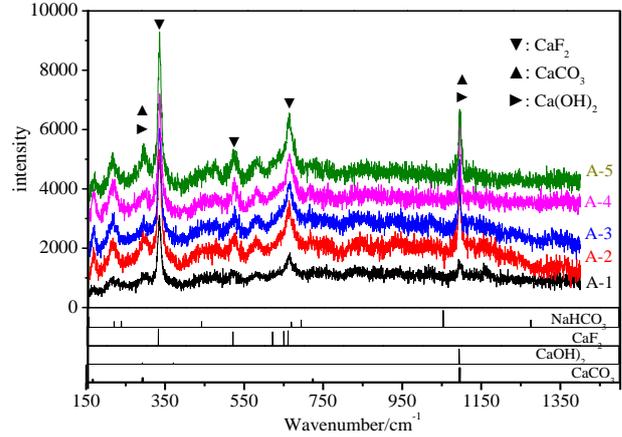


Fig. 4. Raman spectra in  $\text{CaF}_2$ - $\text{HCO}_3$ - $\text{OH}$  solution

It can be seen from the Raman spectrum that the solid part mainly includes  $\text{CaF}_2$ ,  $\text{CaCO}_3$ ,  $\text{Ca}(\text{OH})_2$ , etc. Therefore, it can be seen that  $\text{Ca}(\text{OH})_2$  and  $\text{CaF}_2$  can undergo a dissolution reaction. Under the disturbance of  $\text{HCO}_3^-$ ,  $\text{Ca}(\text{OH})_2$  gradually decreased and eventually disappeared, thus becoming a  $\text{CaF}_2$ - $\text{HCO}_3$  system:

$\text{HCO}_3^-$  can react with  $\text{H}_2\text{O}$  chemically to form a hydrolysis reaction, and can also undergo an electrolysis reaction,  $\text{Ca}^{2+}$  can react with  $\text{CO}_3^{2-}$  to form a precipitation Eq. 9:

1. The calcium ion in the solution should be equal to the amount of  $\text{Ca}^{2+}$  dissolved in  $\text{CaF}_2$  minus the amount of  $\text{Ca}^{2+}$  ion formed in  $\text{CaCO}_3$ .

$$C_{Ca} = \frac{1}{2}C_F - C_{\text{CaCO}_3}. \quad (13)$$

2. Conservation of carbon.

$$C_{\text{CaCO}_3} = C_{\text{HCO}_3(\text{T})} - C_{\text{H}_2\text{CO}_3} - C_{\text{HCO}_3} - C_{\text{CO}_3}. \quad (14)$$

3. Charge equilibrium.

$$C_H + C_{\text{Na}} + 2C_{Ca} = C_{\text{HCO}_3} + 2C_{\text{CO}_3} + C_{\text{OH}} + C_F; \quad (15)$$

$$(C_{\text{OH}})^2 \frac{K_w}{C_{\text{OH}}} + \frac{K_2}{(C_{\text{OH}})^2} \frac{K_w}{K_3} \frac{K_{\text{CC}}}{C_{Ca}} (C_{\text{OH}})^2 = \quad (16)$$

$$\frac{K_{\text{CC}}}{C_{Ca}} (C_{\text{OH}})^2 + C_{\text{OH}} (C_{\text{OH}})^2 + \frac{1}{2} \sqrt{\frac{K_{\text{CF}}}{C_{Ca}}} (C_{\text{OH}})^2 - C_{Ca} (C_{\text{OH}})^2$$

After calculation, it can be calculated by Euler formula, and the results were shown in Fig. 5. It can be seen that the theoretical and practical results are in good agreement, that is, with the increase of  $\text{HCO}_3^-$  concentration, the value of pF in  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3$  system gradually decreased, that was, the dissolved  $\text{F}^-$  anion concentration gradually

increased. Therefore,  $\text{HCO}_3^-$  in solution can promote the dissolution of  $\text{F}^-$  anions.

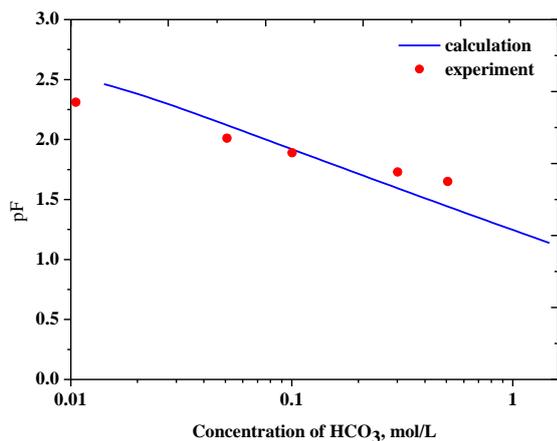


Fig. 5. pH in  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$  system solution

#### 4. CONCLUSIONS

By simulating the chemical system of phosphogypsum solidified in cement-based cementing materials, the concentration of  $\text{F}^-$  anion in the system was studied by chemical analysis and thermodynamic equation, and the changes of solid chemical products were studied by laser Raman spectroscopy.

1.  $\text{CaF}_2$  was a insoluble compound. Because of the same ion effect, the existence of  $\text{Ca}(\text{OH})_2$  led to a significant reduction in the  $\text{F}^-$  anion concentration of  $\text{CaF}_2$ .
2. In  $\text{Ca}(\text{OH})_2$ - $\text{CaF}_2$ - $\text{HCO}_3^-$  system and  $\text{CaF}_2$ - $\text{HCO}_3^-$ -OH system, with the increase of  $\text{HCO}_3^-$  concentration, the concentration of dissolved  $\text{F}^-$  anions gradually increased. Therefore,  $\text{HCO}_3^-$  in solution can promote the dissolution of  $\text{F}^-$  anions.

Therefore, the solidified  $\text{CaF}_2$  in cement-based materials faced a risk of dissolution, which requires attention in groundwater environments containing  $\text{HCO}_3^-$  anions.

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