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 Ca(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 CaF_2. These cement-based materials often serve in environments containing carbonate groundwater, which changes the stability of solidified CaF_2. This paper studied the solid and liquid changes in Ca(OH)_2-CaF_2, Ca(OH)_2-CaF_2-HCO_3, CaF_2-HCO_3-OH systems, and therefore studied the solubility of the by-product CaF_2 of phosphogypsum in the groundwater containing HCO_3 anion after curing in the cement-based cementitious system through experiments and thermodynamic equation simulation. The results showed that the dissolved Ca^2+ of Ca(OH)_2 led to the dissolution of CaF_2, which led to a significant reduction in the F^- anion concentration. However, with the increase of HCO_3 concentration in groundwater, the F^- anion concentration of Ca(OH)_2-CaF_2-HCO_3 system increased, and the main product formed in the solid phase was calcium carbonate; The dissolution of F^- anions in CaF_2-HCO_3-OH system also increased with the increase of HCO_3 concentration. Therefore, the influence of 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 phosporous chemical industry. The main component of phosphogypsum is CaSO_4•2H_2O 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, 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 P_2O_5, 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 phosphorous 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 (P_2O_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 Ca(OH)_2 admixture was added, impurities such as soluble F^- and P_2O_5 can be neutralized [9]. S. Liu found that the minimum requirement for Ca(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 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 β-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 P_2O_5 and 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
During the investigation of groundwater, HCO$_3$- anion was during service, especially the erosion of flowing water. Based materials can encounter the impact of groundwater which the alkaline substance was mainly Ca(OH)$_2$. When Ca$_2^+$ ions in the Ca(OH)$_2$ were depleted, Ca(OH)$_2$ was added to cement clinker, lime was added for pretreatment, so that the soluble ions in phosphogypsum can be converted into Ca$_3$(PO$_4$)$_2$ and 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 CaSO$_4$·2H$_2$O in phosphogypsum was consumed as a retarder in cement-based materials to form ettringite, the most other ions were mainly fluoride anions, forming 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, HCO$_3$- anion was a common anion found in groundwater [18]. It can precipitate with Ca$^{2+}$ ion, which may promote the dissolution of solidified 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 Ca(OH)$_2$. When cement-based materials encountered groundwater containing HCO$_3$- anion, Ca(OH)$_2$ in cement-based materials formed a complex chemical system with phosphogypsum and HCO$_3$- in groundwater, which constituted the Ca(OH)$_2$-CaF$_2$-HCO$_3$ system. When the Ca$^{2+}$ ions in the Ca(OH)$_2$ were depleted, Ca(OH)$_2$ was converted to OH$^-$, resulting in the formation of a CaF$_2$-HCO$_3$-OH system. Therefore, Ca(OH)$_2$-CaF$_2$-HCO$_3$ and CaF$_2$-HCO$_3$-OH systems were used to study the stability of CaF$_2$ internally solidified during the early and late dissolution processes of cement-based materials under the influence of 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 Ca(OH)$_2$ (Damao chemical reagent plant, AR) was used for simulation research; The solidified fluoride ions were directly studied using the chemical reagent CaF$_2$ (Sinopharm Chemical ReagentCo., Ltd, AR); The study of bicarbonate ions in groundwater using the chemical reagent NaHCO$_3$ (Sinopharm Chemical ReagentCo., Ltd, AR); The alkaline environment of the system is regulated using NaOH (Sinopharm Chemical ReagentCo., Ltd, AR); Distilled water.

2.1.2. Proportion of mixture

In the early stage, Ca(OH)$_2$ was mainly dissolved in cement-based materials, and the solidified CaF$_2$ and HCO$_3$- in groundwater jointly formed the Ca(OH)$_2$-CaF$_2$-HCO$_3$ system; When the Ca$^{2+}$ ions are consumed, the CaF$_2$-HCO$_3$-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

<table>
<thead>
<tr>
<th>System</th>
<th>CaF$_2$, g</th>
<th>NaOH, g</th>
<th>Ca(OH)$_2$, g</th>
<th>NaHCO$_3$, g</th>
<th>Water, mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(OH)$_2$-CaF$_2$-HCO$_3$</td>
<td>2.5</td>
<td>0</td>
<td>2.5</td>
<td>5.04</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0</td>
<td>2.5</td>
<td>10.08</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0</td>
<td>2.5</td>
<td>15.12</td>
<td>150</td>
</tr>
<tr>
<td>CaF$_2$-HCO$_3$-OH</td>
<td>2.5</td>
<td>0.080</td>
<td>0</td>
<td>0.177</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.080</td>
<td>0</td>
<td>0.856</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.080</td>
<td>0</td>
<td>1.687</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.080</td>
<td>0</td>
<td>5.059</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>0.080</td>
<td>0</td>
<td>8.523</td>
<td>150</td>
</tr>
</tbody>
</table>

2.2. Experimental methods

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

By mixing and stirring Ca(OH)$_2$, CaF$_2$, NaHCO$_3$, NaOH and water according to the proportion of mixture in Table 1, and after the ion concentration stabilized, the concentration of 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 CaF$_2$, Ca(OH)$_2$ and NaHCO$_3$

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

\[
CaF_2 = Ca^{2+} + 2F^-; \quad K_{CF} = C_{ca} \cdot C_{F}^2
\]

\[
Ca(OH)_2 = Ca^{2+} + 2OH^-; \quad K_{cOH} = C_{ca} \cdot C_{OH}^2
\]

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

Thermodynamic equilibrium constants of reactions were from Ref. [19]. After calculation, the Ca$^{2+}$ ion
concentration of saturated CaF₂ after equilibrium was 0.001098 mol/L, and F⁻ anion concentration was 0.002197 mol/L; and Ca²⁺ ions concentration of Ca(OH)₂ after equilibrium was 0.011 mol/L, and the OH⁻ anion concentration was 0.022 mol/L.

HCO₃⁻ can react with H₂O chemically to form a hydrolysis reaction, and can also undergo electrolysis reaction:

\[ HCO_3^- + \text{H}_2\text{O} = \text{H}_2\text{CO}_3 + \text{OH}^- \qquad (3) \]

\[ C_{\text{HCO}_3} \cdot K_w = C_{\text{H}_2\text{CO}_3} \cdot C_{\text{OH}^-} \]  

\[ \text{H}^+ + \text{OH}^- = \text{H}_2\text{O} ; C_{\text{H}^+} = \frac{K_w}{C_{\text{OH}^-}} \qquad (5) \]

where K₂, K₃ and Kw were the standard equilibrium constant of Eq. 3, Eq. 4 and Eq. 5, respectively; C₃H₂CO₃, C₃HCO₃, C₄H and C₃CO₂ were the concentration of H₂CO₃, HCO₃⁻, H⁺ and CO₃²⁻ respectively when the system reached chemical equilibrium.

It can be seen that HCO₃⁻ can lead to an increase in the concentration of OH⁻ in the solution through hydrolysis, that was, to an increase in the pH of the solution; however, HCO₃⁻ can form more H⁺ through ionization, which led to lower pH of the system; therefore, the pH of HCO₃⁻ solution was the result of hydrolysis and ionization. The relationship between the pH of the solution and the added HCO₃⁻ in the equilibrium state can be obtained by calculating Eq. 3 – Eq. 5, and the result was shown in Eq. 6:

\[ C_{\text{HCO}_3}(T) = \frac{[\{C_{\text{H}_2\text{CO}_3}\}^2 - K_w] [K_1 (C_{\text{H}_2\text{CO}_3})^2 + K_2 K_w + K_w C_{\text{OH}^-}]}{K_2 K_w C_{\text{OH}^-} - K_w (C_{\text{H}_2\text{CO}_3})^2} \cdot (6) \]

Among them, \( C_{\text{HCO}_3}(T) \) was the concentration of total HCO₃⁻ anions added to the system. The relationship between HCO₃⁻ and pH in Fig. 1 can be obtained by the calculation of Eq. 6.

3.2. Calculation of critical concentration of Ca(OH)₂-CaF₂ system

If there was no disturbance of HCO₃⁻ in the system, Ca(OH)₂ and CaF₂ as insoluble substances can not react with each other, and there was only solution-precipitation equilibrium between them. CaF₂ exist in the solution-precipitation equilibrium of Eq. 1; and Ca(OH)₂ exist in the equilibrium of Eq. 2. In the Ca(OH)₂-CaF₂ system, there were three kinds of ions: Ca²⁺, OH⁻, F⁻, and the relationship was:

\[ C_{\text{Ca}^2+} = \frac{1}{2} C_{\text{OH}^-} + \frac{1}{2} C_F^{-} \qquad (7) \]

Combining Eq. 1 and Eq. 2, Eq. 7 can be solved. After calculation, the Ca²⁺ ion concentration of Ca(OH)₂-CaF₂ system after equilibrium was 0.0113 mol/L, while the F⁻ anion concentration was 6.83 × 10⁻⁴ mol/L, OH⁻ anion concentration was 0.022 mol/L (pH = 12.34). Therefore, it can be seen that under the Ca(OH)₂-CaF₂ system, Ca²⁺ ion concentration and OH⁻ anion concentration in the system had little change, but the dissolved amount of F⁻ anion concentration in the system had decreased significantly. This was due to Le Chatelier’s principle [20], the solubility of Ca(OH)₂ was large, and the dissolved Ca²⁺ ion concentration led to the dissolution of CaF₂, which led to a significant reduction in the F⁻ anion concentration.

3.3. Detection of Raman spectroscopy and critical concentration of Ca(OH)₂-CaF₂-HCO₃ system

After mixing Ca(OH)₂, CaF₂ and NaHCO₃ and fully stirring, the corresponding solid part was dried for Raman spectroscopy, and the results were shown in Fig. 2.

![Raman spectra in Ca(OH)₂-CaF₂-HCO₃ solution](image)

Fig. 2. Raman spectra in Ca(OH)₂-CaF₂-HCO₃ solution

It can be seen from the Raman spectrum that the solid part mainly includes CaF₂, CaCO₃, Ca(OH)₂, etc. Therefore, it can be seen that Ca(OH)₂ and CaF₂ can undergo dissolution reaction in an aqueous solution, while under the disturbance of HCO₃⁻ 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. HCO₃⁻ can react with OH⁻ to form a neutralization reaction:

\[ \text{HCO}_3^- + \text{OH}^- = \text{CO}_3^{2-} + \text{H}_2\text{O} \ ; K_i = \frac{C_{\text{CO}_3^{2-}}}{C_{\text{HCO}_3^-} \cdot C_{\text{OH}^-}} \qquad (8) \]
2. The formed CO$_3^{2-}$ precipitated with the dissolved Ca$^{2+}$ of Ca(OH)$_2$ and CaF$_2$:

$$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$$

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

In the Ca(OH)$_2$-CaF$_2$-HCO$_3$ system, there were five ions such as Ca$^{2+}$, OH$^-$, F$^-$, HCO$_3^-$, 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 Ca$^{2+}$ dissolved in Ca(OH)$_2$ and CaF$_2$ minus the amount of Ca$^{2+}$ formed in CaCO$_3$, where the Ca$^{2+}$ dissolved in Ca(OH)$_2$ can be equal to half of the dissolved OH$^-$ anions, and the calcium ions dissolved in CaF$_2$ can be equal to half of the dissolved F$^-$ anions:

$$C_{Ca} = \frac{1}{2} C_{OH}^+ - \frac{1}{2} C_{CO}_3^- - \frac{1}{2} C_F^-$$

(10)

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

2. Carbon element equilibrium.

The amount of HCO$_3^-$ anions in the solution ($C_{HCO}_3$) should be equal to the total amount of HCO$_3^-$ anions ($C_{HCO}_3(T)$) minus the amount of CO$^3_2$ anions minus the amount of Ca$^{2+}$ ion formed by CaCO$_3$. 

$$C_{HCO}_3 = C_{HCO}_3(T) - C_{CO}_3 - C_{Ca}$$

(11)

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

$$C_{HCO}_3(T) = \frac{K_{HCO}_3 + K_{CO}_3 + K_{CC} + 2K_{CC} C_{Ca}}{\sqrt{C_{Ca} C_{CO}_3 C_{HCO}_3(T)}}$$

(12)

3. Charge equilibrium.

Combining Eqs. 1 and 2, Eq. 3 and Eq. 4 into Eq. 5 and Eq. 6 can be solved.

$$C_{Ca} = \frac{1}{2} C_F^- - C_{CaCO}_3$$

(13)


$$C_{CaCO}_3 = C_{HCO}_3(T) - C_{HCO}_3 - C_{CO}_3 - C_{Ca}$$

(14)

3. Charge equilibrium.

$$C_{Ca} + 2C_{Ca} = C_{HCO}_3 + 2C_{CO}_3 + C_{OH}^- + C_F^-$$

$$\left(\frac{C_{Oh}^-}{C_{Oh}^+}\right)^2 + \left(\frac{C_{Ca}^+}{C_{Ca}^-}\right)^2 = \frac{K_{CC} C_{Ca}}{K_{Ca} C_{Ca}}$$

(15)

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

(16)

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 HCO$_3^-$ concentration, the value of pF in Ca(OH)$_2$-CaF$_2$-HCO$_3$ system gradually decreased, that was, the dissolved F$^-$ ion concentration gradually increased. Therefore, HCO$_3^-$ in the solution can promote the dissolution of F$^-$ anions in Ca(OH)$_2$-CaF$_2$-HCO$_3$ system.

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

After mixing NaOH, CaF$_2$ and NaHCO$_3$ and fully stirring, the corresponding solid part was dried for Raman spectroscopy, and the results were shown in Fig. 4.
increased. Therefore, HCO$_3^-$ in solution can promote the dissolution of F$^-$ anions.

Fig. 5. pF in Ca(OH)$_2$-CaF$_2$-HCO$_3^-$ system solution

4. CONCLUSIONS

By simulating the chemical system of phosphogypsum solidified in cement-based cementing materials, the concentration of 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. CaF$_2$ was an insoluble compound. Because of the same ion effect, the existence of Ca(OH)$_2$ led to a significant reduction in the F$^-$ anion concentration of CaF$_2$.
2. In Ca(OH)$_2$-CaF$_2$-HCO$_3^-$ system and CaF$_2$-HCO$_3^-$-OH system, with the increase of HCO$_3^-$ concentration, the concentration of dissolved F$^-$ anions gradually increased. Therefore, HCO$_3^-$ in solution can promote the dissolution of F$^-$ anions.

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

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