



## Solid–liquid equilibrium curve of calcium in 6 mol/L ammonium nitrate solution



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### ARTICLE INFO

#### Article history:

Received 17 February 2013

Accepted 3 June 2013

#### Keywords:

Calcium leaching  
Acceleration (A)  
Cement paste (D)  
Nitrate (D)

### ABSTRACT

Calcium leaching of cement-based materials is of concern for scientific and application significance. Solid–liquid equilibrium curve of calcium is crucial for understanding the calcium leaching mechanism and for calcium leaching modeling. Solid–liquid equilibrium curve of Portland cement system in 6 mol/L ammonium nitrate solution is experimentally obtained using the dissolving equilibrium between cement paste powders and simulated pore solutions. The obtained equilibrium curve in nitrate solution has a similar three-stage form to that in water, but the concentrations of dissolved calcium increase up to two orders of magnitude, which is the main acceleration mechanism for calcium leaching. Besides the solid–liquid equilibrium curve of calcium, the equilibrium curves between other solid elements (including sulfur, aluminum, manganese, iron) and dissolved calcium are presented. It is found that sulfur and manganese are also leached in three stages, but aluminum and iron are not leachable.

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## 1. Introduction

### 1.1. Calcium leaching of cement-based materials

Calcium (Ca) leaching of cement-based materials is of concern in the structures used for radioactive waste disposal containers, underground pipes, dams, and water tanks that are constantly composed to the low pH environment. Generally speaking, the concentration gradients between the pore solution and the environment water lead to diffusion of dissolved Ca from the pore solution to the surrounding water. Once the concentration of pore solution is reduced, the Ca in solid skeleton, mainly the calcium hydroxide (CH) and calcium–silicate–hydrate (C–S–H), will dissolve gradually. These processes will increase the porosity, consequently increase the permeability and decrease the strength of the cement matrix (such as in [1–10]). For modeling research of Ca leaching, most of the investigations use the solid–liquid equilibrium curve to describe the dissolution process, and use the diffusion to describe the transport process (such as in [2,4,6]). All these models strongly depend on the solid–liquid equilibrium curve, which describes the solubility of cement hydration product and controls the Ca dissolving and leaching processes.

Experimentally, it was reported that the leaching front of concrete submerged in still field water for 100 years was only about 5 to 10 mm [11,12]. Considering the time consuming of the field water,

most of the laboratory tests applied accelerated leaching protocols with different accelerated methods, mainly 6 mol/L (6 M) ammonium nitrate solution [7–10,13–18], ammonium chloride solution [19], deionized water [13,20–24], and electrochemical method [25,26]. Among these methods, 6 M ammonium nitrate solution, which can accelerate the leaching speed two orders while still get the same end products [17], is the most effective method and has been intensively used to experimentally investigate Ca leaching behavior.

### 1.2. Solid–liquid equilibrium curve of Ca in water

The solid–liquid equilibrium curve of Ca in water stems from the equilibrium in the CaO–SiO<sub>2</sub>–H<sub>2</sub>O system. Since Le Chatelier's classic studies on C–S–H in the 1880s [27], there have been numerous investigations on the dissolving equilibrium of C–S–H or cement paste at room temperature (such as in refs [28–32]).

Because dissolution is much faster than diffusion in the leaching process of cement-based materials, Buil [2] firstly applied the solid–liquid equilibrium curve to model the leaching process in 1992, where the solid–liquid equilibrium curve was used to relate the Ca in solid skeleton  $s$  and the Ca dissolved in pore solution  $c$ . Berner [3] also raised the equilibrium curve to describe the dissolution behavior of hydrated cement in 1992. Since that, the equilibrium curve has been applied to build Ca leaching models or to explain the leaching phenomenon in numerous studies (such as in [6,16,19,21–23]). The original Buil's equilibrium curve is mathematically simple and with reasonable accuracy. The equilibrium curve has been slightly modified in later research. One typical modified equilibrium curve [16,19] is expressed by Eq. (1), and the corresponded equilibrium

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curve [16] was compared with the initial equilibrium curve by Buil [2] in Fig. 1.

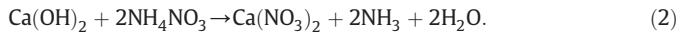
$$cs = \begin{cases} \left( \frac{-2}{x_1^3} c^3 + \frac{3}{x_1^2} c^2 \right) \left\{ C_{CSH} \left( \frac{c}{c^{eq}} \right)^{1/3} \right\} & 0 \leq c \leq x_1 \\ \left\{ C_{CSH} \left( \frac{c}{c^{eq}} \right)^{1/3} \right\} & x_1 < c \leq x_2 \\ \left\{ C_{CSH} \left( \frac{c}{c^{eq}} \right)^{1/3} \right\} + \frac{C_{CH}}{(c^{eq} - x_2)^3} (c - x_2)^3 & x_2 < c \leq c^{eq} \end{cases} \quad (1)$$

where  $x_1$  is the Ca concentration in pore solution when C–S–H dissolves quickly (mmol/L);  $x_2$  is the Ca concentration in pore solution when CH has completely dissolved, and C–S–H begins to dissolve (mmol/L);  $c^{eq}$  is the saturated concentration of dissolved Ca in deionized water under normal temperature (mmol/L). Normally  $x_1$  is taken as 2 mmol/L [16,19],  $x_2$  is taken as  $(c^{eq} - 3)$  mmol/L [16,19] or  $(c^{eq} - 1)$  mmol/L [21–23], and  $c^{eq}$  is taken as 20 mmol/L [16,19] or 22 mmol/L [21–23].

According to Eq. (1) and Fig. 1, the dissolving and leaching processes in water can be interpreted as the following three stages. In the first stage ( $x_2 < c < c^{eq}$ ), CH is quickly dissolved and leached. In the second slow and central stage ( $x_1 < c < x_2$ ), the Ca in C–S–H is partially dissolved and leached, resulted Ca/Si molar ratio (Ca/Si) in C–S–H from about 1.6 to about 0.8 [29]. It is still in this second period, the Ca in sulfoaluminates is dissolved and leached [7,21]. In the third stage ( $0 < c < x_1$ ), when the Ca concentration in pore solution is less than  $x_1$ , about 2 mmol/L, the partially leached C–S–H is quickly and totally decalcified to be silica gel (such as in [3,6]).

### 1.3. Solubility in ammonium nitrate solution and unsettled questions

The dissolution of CH in ammonium nitrate solution can be written according to the following chemical reaction [8]:



For the dissolution of C–S–H, a similar reaction equation is followed. The gaseous reaction product  $NH_3$  and the high solubility of reaction product calcium nitrate favor the reaction process greatly. And the high Ca concentration due to high solubility of calcium nitrate changes the equilibrium curve and increases the concentration gradient.

Several papers have investigated the accelerated Ca leaching of cement paste in 6 M ammonium nitrate solution. At room temperature, the saturated Ca concentration in the pore solution of cement paste is only about 20 mmol/L in water, while it is reported to be 2730 mmol/L [6] or 2900 mmol/L [8] in 6 M ammonium nitrate solution. For  $x_1$  and  $x_2$ , Tognazzi [18] thinks that  $x_1$  does not change while  $x_2$  changes to a value close to 2730 mmol/L; Gerard et al. [6] think that both  $x_1$  and  $x_2$  do not change (still in the range of 0–20 mmol/L), and that the main acceleration effect is controlled by the magnifying factor of 60 on the

effective diffusion coefficient; Wan et al. [16] think that both  $x_1$  and  $x_2$  change and they take  $x_1$  as 273 mmol/L and  $x_2$  as 2320 mmol/L in their equilibrium curve in 6 M ammonium nitrate solution. Pichler et al. [7] propose a simple linear equilibrium curve in their acceleration model. Besides, debate exists on whether sulfoaluminates is leachable or not in 6 M ammonium nitrate solution (such as in [7,33–35]).

Although 6 M ammonium nitrate solution is widely applied for Ca leaching research, several issues concerned the equilibrium curve in 6 M ammonium nitrate solution remain unsettled: (i) does the equilibrium curve in 6 M ammonium nitrate solution still keep the three-stage form as that in water; (ii) if it keeps the same form as that in water, what are the values of  $x_1$ ,  $x_2$  and saturated concentration  $c^{eq}$ ; (iii) does the sulfoaluminates leach in 6 M ammonium nitrate solution?

### 1.4. Current study

To clarify the accelerated Ca leaching process and the acceleration mechanism, this research focuses mainly on the solid–liquid equilibrium curve of Ca in 6 M ammonium nitrate solution. Special experiments are designed to obtain this equilibrium curve. Once the equilibrium curve is experimentally obtained, the several unsettled questions stated in Section 1.3 can be answered.

## 2. Experimental

### 2.1. Experimental design

The solid–liquid equilibrium curve of Ca in water is one kind of phase diagram [1,2,17]. Considering that Ca leaching in 6 M ammonium nitrate solution is still a diffusion controlling process and a dynamic equilibrium between  $s$  and  $c$  still holds, the solid–liquid equilibrium curve of Ca in 6 M ammonium nitrate solution is also one kind of phase diagram. When cement-based materials are exposed in 6 M ammonium nitrate solution for a long time, dynamic equilibrium will be established, and concentration gradients of different ions will form in pore solution finally. Considering that the free  $K^+$  and  $Na^+$  leach very quickly, only after a short leach period, the influence of these free  $K^+/Na^+$  can be neglected, so the main ions in pore solution are only  $Ca^{2+}$ ,  $NH_4^+$  and  $NO_3^-$  which keep ionic charge neutral. Just as the solid–liquid equilibrium curve in water describes the equilibrium of water ( $H^+$ ,  $OH^-$ )-dissolved Ca-solid hydrated product, the solid–liquid equilibrium curve in 6 M ammonium nitrate solution describes the equilibrium of 6 M ammonium nitrate solution ( $NH_4^+$ ,  $NO_3^-$ )-dissolved Ca-solid hydrated product.

As illustrated in Fig. 2, from the leaching surface to the leaching front, the  $Ca^{2+}$  concentration will increase because of diffusion of Ca from the inner part to the surface, while the  $NH_4^+$  concentration will decrease because of chemical reactions. Now let us consider the boundary conditions of the ion concentrations in pore solution. On

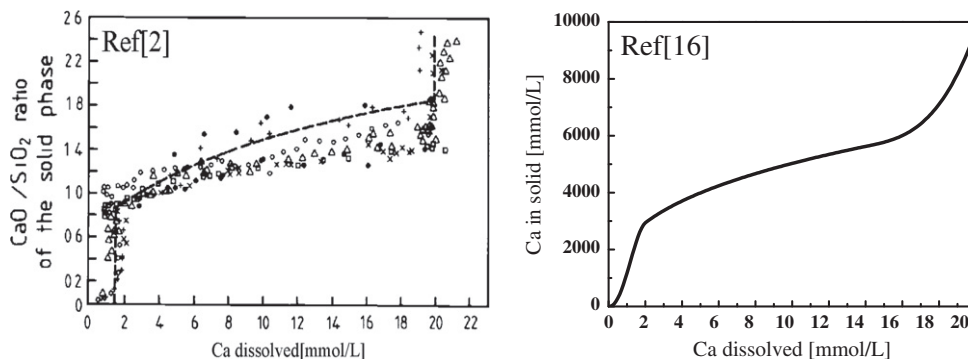


Fig. 1. Ref [2]: the collected dissolution data and the proposed solid–liquid equilibrium curve in water taken from reference [2]; Ref [16]: the modeling solid–liquid equilibrium curve in water taken from reference [16].

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