



Dissolution and leaching mechanisms of calcium ions in cement based materials [☆]



Xuebing Wang ^{a,*}, Kangning Xu ^b, Yexue Li ^a, Shengbo Guo ^a

^a School of Civil Engineering and Architecture, Hubei University of Arts and Science, Xiangyang 441053, China

^b School of Medical, Xiangyang Vocational and Technical College, Xiangyang 441021, China

HIGHLIGHTS

- The main factor in the early dissolution process was chemical dissolution processes.
- Chemical reaction kinetics was modeling based on mechanism of dissolution and leaching.
- Chemical mechanism model was used to verification the influence of w/c and SCM.

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ABSTRACT

Dissolution and leaching mechanism of the calcium ions in cement based material has an important influence on its service performance. In this paper, the mechanism of the dissolution and leaching process of cement based materials was analyzed. The results showed that early dissolution and leaching behavior of cement-based materials was different with the later period, and therefore this paper was just focus on the early dissolution. At the early period of dissolution and leaching, it was mainly due to the chemical dissolution process by discussing the mechanism of this period; moreover, mathematics mechanism of early dissolution of calcium in cement based materials was determined by using chemical kinetics combined with mathematic calculated, and the chemical mechanism model was then verified by using the literature data.

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1. Introduction

Cement based materials, such as cement mortar and concrete, were all spliced together by the hydration of cement [1]. As the adhesive material, cement was played the very important role. The hydration products which were including C-S-H, Ca(OH)₂, ettringite and C-A-H, etc [2]. Were eventually induced hardened, and improved the strength of materials gradually [3].

Ca element was a main part in all of these hydration products, and the changes of it was affected the stability of all hydrated products. The proportion of Ca elements in C-S-H was determined the performance of C-S-H, generally speaking, C-S-H was formed by the aggregation of many [SiO₄]⁴⁻ tetrahedral surrounding on the CaO_x polyhedron layers [4], Ca²⁺ was the important element of constituent part of frame structure of C-S-H. Therefore, the loss

of Ca²⁺ would cause the stability of C-S-H to be decreased, and the calcium rich type C-S-H would gradually turn into the silicon rich C-S-H [5]; other product Ca(OH)₂ was mainly composed of crystal shape in the pore of materials, it was easy to be dissolved with the decreased of Ca²⁺. When Ca(OH)₂ was dissolved, the strength of the cement-based material was decreases gradually [6] (Fig. 1); the stability of ettringite was also related with Ca²⁺ ion of the pore solution [4], if Ca²⁺ was leaching from pore solution, the balance of ettringite crystal and related ions was changed, so it would finally change the stability of ettringite [7]. As the changes of content of Ca²⁺ in system of cement-based material can affected the stability of all the hydration product, therefore it can finally change the physical performances of cement based materials.

In the service period of cement-based materials, the dissolution of Ca²⁺ ions was also seriously affected their service performance. Generally, most of the chemical corrosion of cement-based materials was participation of Ca²⁺ ions, such as SO₄²⁻ corrosion, Cl⁻ anion corrosion and carbonization. SO₄²⁻ anion was reacted with Ca²⁺ ions and ultimately ettringite and gypsum etc. were formed in this process [8]; Cl⁻ anion corrosion was also reacted with Ca²⁺ ions to

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* Corresponding author.

E-mail address: wangxuebing@hbuas.edu.cn (X. Wang).

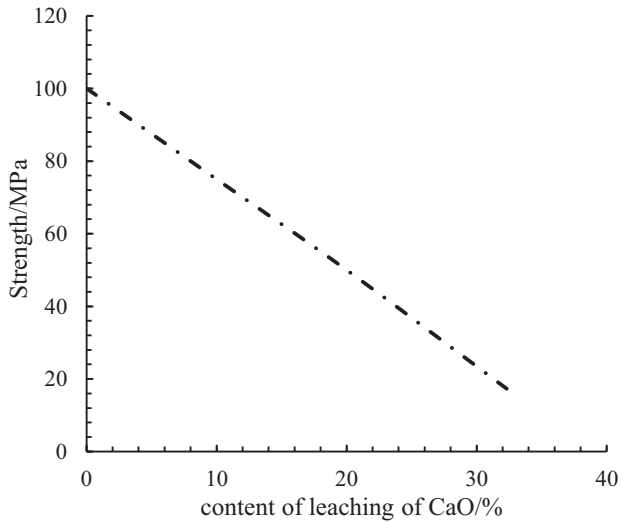


Fig. 1. Relationship between content of leaching of $\text{Ca}(\text{OH})_2$ and strength of concrete [6].

form CaCl_2 [6]; CO_2 was reacted in this system and the pH of pore solution of cement based material was decreased and CaCO_3 was follow formed [9]. These chemical reactions were all related to the dissolution of Ca^{2+} ions, rate of dissolution of Ca^{2+} of materials was related to the rate of chemical corrosion of cement based material and finally affect the durability of materials.

The dissolved sources of Ca^{2+} ions was mainly derived from $\text{Ca}(\text{OH})_2$ and C-S-H formed by hydration of cement, therefore the content of $\text{Ca}(\text{OH})_2$ was related to the composition of cement. In general, cement based material not only had cement clinker, but also SCM such as fly ash, slag powder, silica fume and so on, some of which contained active SiO_2 or Al_2O_3 and had property of potential cementitious, which can reacted with $\text{Ca}(\text{OH})_2$ and eventually formed C-S-H. In this process, $\text{Ca}(\text{OH})_2$ was gradually be consumed and its content was eventually reduced [10].

It was generally believed that the dissolution of calcium ions with time was in accordance with the following expression [11–13]:

$$N(t) = a_1 \cdot \sqrt{t} + b_1 \quad (1)$$

$N(t)$ represented the sum of all dissolved Ca^{2+} ions; t was for time; a_1 and b_1 was the constant respectively.

Because the experiment of dissolved Ca^{2+} ion in different layer of materials was not easy to be detected, so the dissolution of Ca^{2+} ions in general literature was focused on the detection of content of total Ca^{2+} ions by leaching process.

2. Leaching mechanism of Ca^{2+}

2.1. Formulation and background

(1) Analysis of theoretical mechanism

In many former researches, the dissolution process of calcium ions was mainly attributed to the diffusion process, in this process, dissolved Ca^{2+} ions was gradually transported to the outside through the diffusion.

For the leaching process of the crystalline $\text{Ca}(\text{OH})_2$, it must be dissolved from crystal firstly; and then the ions can be gradually diffused into the solution out of material. In first process, due to low solubility of $\text{Ca}(\text{OH})_2$ of which its solubility product constant of K_{sp} was 5.5×10^{-6} [14], Ca^{2+} ions were dissolved from $\text{Ca}(\text{OH})_2$ which accompanied by dissolution of OH^- anions. In cement

based materials, the pore solution was a saturated solution of $\text{Ca}(\text{OH})_2$, so the pH value of pore solution in cement-based material was about 12.5–13.5, therefore the upper limit concentration of Ca^{2+} ion was about 0.000055–0.0055 mol/L according to the solubility rule. In this period, even some Ca^{2+} was leached from pore solution, $\text{Ca}(\text{OH})_2$ and C-S-H can dissolve and supply some Ca^{2+} . However, in the later diffusion stage, the dissolution of $\text{Ca}(\text{OH})_2$ cannot supply the loss of Ca^{2+} ion and lead to decrease of Ca^{2+} in pore solution due to the decreased of crystalline $\text{Ca}(\text{OH})_2$, so the process in the early and late stages was different. Which was the main factor in the early process between the chemical dissolution processes and the diffusion process in early dissolution stage?

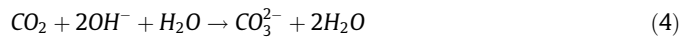
When ions was diffused in a dilute solution, the influence factors can be calculated by the Stokes-Einstein equation [15]:

$$D_0 = \frac{k_B T}{6\pi\mu R_0} \quad (2)$$

It can be seen that the diffusion coefficient of ions was related to the temperature (T), the viscosity of the solution (μ) and radius of the ion (R_0), k_B was Boltzmann constant. According the data of Lange's handbook of chemistry, effective radius of OH^- and Ca^{2+} was 3.5 Å and 6 Å respectively [14], therefore diffusion coefficient of OH^- anion was larger than Ca^{2+} ions. Diffusion process was always in line with the Fick's second law which was [16]:

$$c(x, t) = c_0 \cdot \text{erfc}\left(\frac{x}{2\sqrt{Dt}}\right) \quad (3)$$

Therefore the concentration of the ions ($c(x, t)$) was related with the initial concentration of ions (c_0) and diffusion coefficient in the same time (t) and depth (x). Firstly, according to this law the concentration of OH^- ions was twice as much as that of the concentration of Ca^{2+} . However, it can be seen from the result E. Rozière et al.'s research that the concentration of OH^- ions was less than double [12]. Even carbonation can decrease the content of OH^- anion in solution, but it can also decrease the content of Ca^{2+} ions:



Therefore carbonation cannot explain the reason of decreased of OH^- .

Secondly, if diffusion process was the main fact in early dissolution stage, the dissolution speed was faster than diffusion, therefore concentration of Ca^{2+} in pore solution can always maintain at a constant, so concentration of leached Ca was directly proportional to the time. However the experimental data was not according to this trend and it was according to Eq. (1).

Thirdly, according to the result of Rozière et al., the leaching depth which lead the disappear of $\text{Ca}(\text{OH})_2$ was less than 0.5 mm after the dissolution of $\text{Ca}(\text{OH})_2$ [12,13]; according to the research results of scanning electron microscopy (SEM), the particle size of $\text{Ca}(\text{OH})_2$ crystal was larger than 10–20 μm [17–19] (Fig. 2), therefore it can be considered that the dissolution of Ca^{2+} at early stage was all happened on surface $\text{Ca}(\text{OH})_2$. Due to the surplus of Ca^{2+} ions some dissolution was happened on the surface of C-S-H.

Diffusion process was not the main factor in early process, and therefore chemical dissolution process was the main factor in this process. According to SEM of cement based materials, some $\text{Ca}(\text{OH})_2$ was formed on the surface of materials, other $\text{Ca}(\text{OH})_2$ was existed in the surface pore, the ions dissolved from these position didn't need to diffuse and quickly leached into solution. Ca element in rich Ca type C-S-H was also dissolved from frame structure of C-S-H. For example, in sulfate attack, especially in occasion of existing of ammonium, more Ca^{2+} ions were dissolved from surface and finally formed into gypsum when SO_4^{2-} anions was existing in the

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