Cement and Concrete Research 59 (2014) 118–138

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Ion-specific effects influencing the dissolution of tricalcium silicate

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ARTICLE INFO

Article history:
Received 22 October 2013
Accepted 26 February 2014
Available online 25 March 2014

Keywords:
Dissolution
Tricalcium silicate
Ion specific
Pitzer equations
Alumino-silicate formation

ABSTRACT

It has been recently demonstrated that the dissolution kinetics of tricalcium silicate (C_3S) is driven by the deviation from its solubility equilibrium. In this article, special attention is paid to ions relevant in cement chemistry likely to interact with C_3S. In order to determine whether specific effects occur at the interface C_3S–water, particular efforts have been made to model ion activities using Pitzer's model. It has been found that monovalent cations and monovalent anions interact very little with the surface of C_3S. On the other side, divalent anions like sulfate slow down the dissolution more strongly by modifying the surface charging of C_3S. Third, aluminate ions covalently bind to surface silicate monomers and inhibit the dissolution in mildly alkaline conditions. The formation and the breaking of these bonds depend on pH and on $[Ca^{2+}]$. Thermodynamic calculations performed using DFT combined with the COSMO-RS solvation method support the experimental findings.

1. Introduction

The dissolution of tricalcium and dicalcium silicates has been recently rationalized with the help of a thermodynamic framework which provided a plausible explanation for the relative low solubility of these phases during their hydration in typical cement conditions [1]. The authors focused on the role of the deviation from the solubility equilibrium, i.e., the activities of calcium, hydroxide and silicate ions, on the dissolution rate of alite (tricalcium silicate or C_3S containing some impurities). In the mentioned article, the ion activities have been calculated within the Debye–Hückel theory which is reliable for moderate ionic strength. A typical cement pore solution is however much more complex and other ions can influence the dissolution of these anhydrous phases. Namely, the solution is rich in alkali and sulfate ions and contains a non-negligible amount of aluminum ions, known for their strong interactions with siliceous surfaces. Also, a large proportion of monovalent anions like nitrate or chloride ions are introduced if some chemical admixtures have been used in order to improve the setting or the hardening properties of the cementitious materials. All these ions constitute a set of factors likely to influence the dissolution rate of tricalcium silicate (C_3S) in cement conditions. If they are established, specific interactions can come from two origins: they might be due to ion–ion interactions in solution or due to some interactions at the interface C_3S–water. The first cause will require a better estimation of the activity coefficients than with the Debye–Hückel framework in order to calculate the deviation from solubility equilibrium. The second cause will lead to stabilization or destabilization of the dissolving surface by ions bound to this one according to two types of bonding: ionic or covalent.

The species in this work are covered in four different sections since categorized in four classes: the alkali ions (Na^+, K^+, Cs^+), the monovalent anions (Cl^-, NO_3^-, etc.), the (divalent) sulfate anions and finally the aluminate anions. Experimentally, we proceeded as previously [1], i.e., the dissolution experiments were performed in diluted-enough conditions undersaturated with respect to most of the hydrates likely to precipitate if higher concentrations would have been used. In these conditions, a pure dissolution regime is observed. The activities of the ions in solution are estimated according to the Debye–Hückel's and Pitzer's models. The last one describes the ion–ion interactions in solution and the comparison between both models allows an appreciation of the importance of the ion-specificity due to these interactions. Ion-specific effects have not been in focus of studies concerned with the dissolution of cement phases although they are important to a wealth of phenomena in biology, chemistry and physics [2–5]. These selective interactions are often ranked into the so-called Hofmeister series which qualitatively describes ion-specificity observed in many experimental fields.

Due to their ability to covalently bind to silicate species, one should distinguish aluminum ions from other ions. Aluminum is dissolved from anhydrous aluminous solid phases but the aluminum concentration remains low in the pore solution because of the low solubility of aluminate hydrates. Its interactions with the cementitious silicate phases

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http://dx.doi.org/10.1016/j.cemconres.2014.02.006
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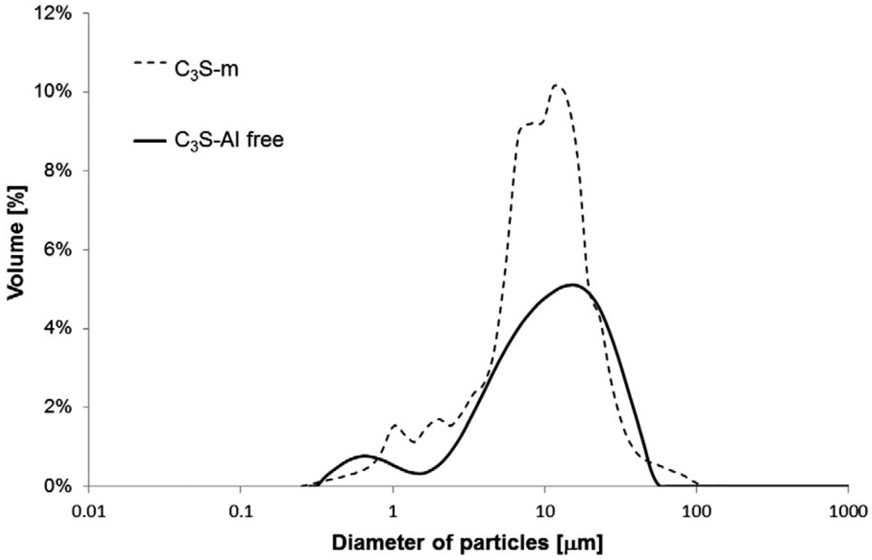

Fig. 1. Grain size distributions of both tricalcium silicates used in this study.

have been long the subject of various studies [6–9]. More generally, it is well recognized that aluminum ions have a perturbing effect on the silicate reactivity [10–14]. Nevertheless, the authors are not aware of any publication on the influence of aluminate ions. In spite of their identification in cement, there is often a lack of thermodynamical data concerning the hydrated alumino-silicate species as well as a thorough description of their structure. In undersaturated conditions [11], it was demonstrated that aluminate ions strongly interact with quartz surfaces and slow down quartz dissolution. A model is proposed which is based on a mechanism involving the co-adsorption of aluminum ions. The identification of hexa-coordinated aluminum species and maybe also penta-coordinated species in similar systems [15,16] indicates that chemical reactions possibly driven by surface effects can occur. The conclusions of Bickmore et al. [11] were drawn from experiments concerning quartz (a tectosilicate) and therefore only usable with utmost care for inosilicates as C$_3$S. Swaddle [17] reviewed the formation of silicate complexes of aluminum. High concentration of these species may be found in alkaline media with a significant lifetime. Nevertheless, due to their large variety, their instability and the lability of aluminum, it is difficult to quantity them. Facing a lack of experimental and thermodynamic data regarding the reactivity of silicate monomers with aluminum ions, we also conducted a modeling work using density functional theory (DFT) in conjunction with the COSMO-RS solvation model to theoretically describe the formation of detected alumino-silicate species and to argue for their thermodynamical stability in conditions encountered in this study.

2. Technical section

2.1. Materials

Two types of tricalcium silicates were used in this study. The first type, with which most of the experiments were carried out, is the same monoclinic polymorph as used in the previous study [1] (denoted C$_3$S-m). Since this polymorph contains a small quantity of aluminum which could be cumbersome for quantitative NMR and XPS measurements of the aluminum amount which has been bound, a pure tricalcium silicate devoid of aluminum was also used. This sample will be noted C$_3$S–

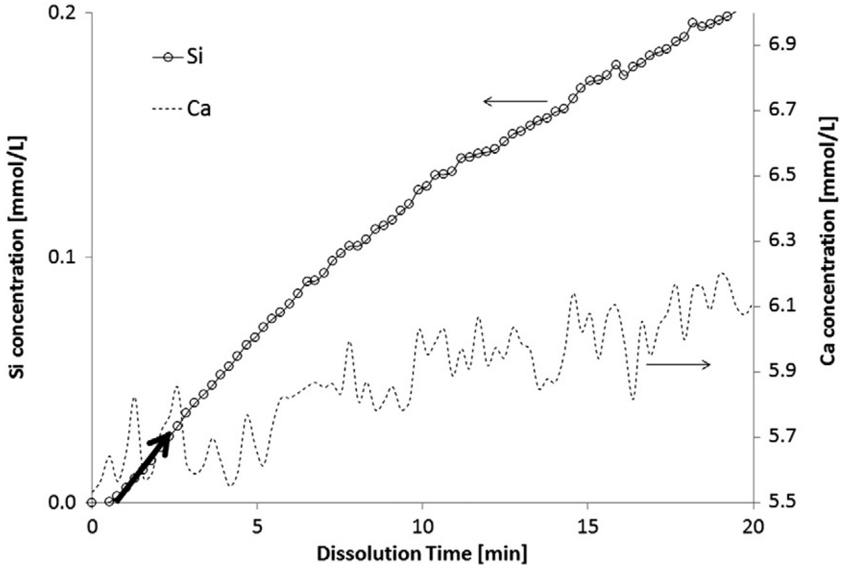

Fig. 2. Evolution of the concentration of Si and Ca during the dissolution of 0.1 g/L C$_3$S-m in 5.5 mM of $Ca(OH)_2$ solution at 20 °C. The bold arrow represents the straight-line used for the determination of the dissolution rate.