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Why alite stops hydrating below 80% relative humidity

Robert J. Flatt ^a, George W. Scherer ^{b,*}, Jeffrey W. Bullard ^c

^a Sika Technology AG, Zürich, Switzerland

^b Princeton University, Eng. Quad. E-319, Princeton NJ 08544, USA

^c National Institute of Standards and Technology, Gaithersburg MD, USA

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ABSTRACT

It has been observed that the hydration of cement paste stops when the relative humidity drops below about 80%. A thermodynamic analysis shows that the capillary pressure exerted at that RH shifts the solubility of tricalcium silicate, so that it is in equilibrium with water. This is a reflection of the chemical shrinkage in this system: according to Le Chatelier's principle, since the volume of the products is less than that of the reactants, a negative (capillary) pressure opposes the reaction.

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1. Introduction

Cement hydration continues to have an intriguing character, surrounded as it is by a number of intensively debated questions. Among the unresolved issues is the reason why hydration of a cement paste stops at a relative humidity of about RH = 0.8, even though the system still contains a significant amount of water [1–5]. For example, Jensen et al. [6] report that triclinic C_3S^1 has a degree of hydration of 36% after 90 days at RH = 0.98, but a degree of hydration of only 2% after 90 days when the RH is lowered to 0.85.

This communication shows that a critical relative humidity, below which hydration should stop, can be defined from a relatively simple thermodynamic treatment. Similar analyses have been attempted in the past. Jensen [7] calculated the vapor pressure at which hydration would stop in the absence of condensed water. He found that extremely low RH was required to establish equilibrium between clinker and various mineral phases (*e.g.*, RH<0.01 for equilibrium between clinker and tobermorite). In the present work, we show that the decrease in water activity needed to arrest hydration results from the negative capillary pressure in the pore liquid at RH \leq 0.8.

2. Theory

The basic idea is that the system stops hydrating if C₃S, C–S–H and CH are all simultaneously in equilibrium. This does not happen when excess water is available; however, as relative humidity decreases, the reduction in water activity can allow this equilibrium to be established.

* Corresponding author. Tel.: +1 609 258 5680.

E-mail address: scherer@princeton.edu (G.W. Scherer).

The results of this analysis are particularly sensitive to the selection of the thermodynamic data. This is especially true for C_3S solubility. Indeed, there are different hypotheses to account for the rapid deceleration of C_3S reaction after contact with water. One suggestion is that dissolution involves a step of surface hydroxylation, so that it is the solubility product of this layer rather than that of bulk C_3S that should be used [8–10]. Recent work suggests that the solubility of this layer is 17 orders of magnitude lower than the one obtained from bulk thermodynamics [11,12], and there still is not universal agreement on the value or meaning of alite solubility product, so much caution is warranted when interpreting the results presented here.

In this communication, we use the same data as Bullard and Flatt [13] who found those data to lead to a good prediction of C_3S hydration kinetics using HydratiCA, a kinetic cellular automaton model [14]. In particular, they correctly capture the kinetics of heat release by C_3S hydration as well as the evolution of ionic concentrations in solution [13].

3. Reactions

The dissolution reaction for C₃S is assumed to be [13]:

$$Ca_3SiO_5 + 3H_2O \Rightarrow 3Ca^{2+} + H_2SiO_4^{2-} + 4OH^-.$$
 (1)

C-S-H is modeled as a mixture of two phases denoted CSH₄=Ca $(OH)_2 \cdot SiO_2 \cdot 3H_2O$ and C_2SH_7 =2Ca $(OH)_2 \cdot SiO_2 \cdot 5H_2O$ with Ca/Si ratios of 1 and 2, respectively [13,14]. For these, the dissolution reactions are:

$$Ca(OH)_2 \cdot SiO_2 \cdot 3H_2O \Rightarrow Ca^{2+} + H_2SiO_4^{2-} + 3H_2O$$
 (2)

¹ We use conventional cement chemistry notation, *e.g.* C = CaO, $S = SiO_2$, $H = H_2O$.

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