Reply to the discussion of the paper “Understanding expansion in calcium sulfoaluminate-belite cements”

Dr. Irvin A Chen
Dr. Craig W Hargis, University of North Florida
Dr. Maria C.G. Juenger, University of Texas at Austin

Available at: https://works.bepress.com/craig-hargis/14/
Discussion

Reply to the discussion of the paper “Understanding expansion in calcium sulfoaluminate-belite cements” by G.L. Valenti, M. Marroccoli, M.L. Pace, A. Telesca

Irvin A. Chen a,1, Craig W. Hargis b,*,2, Maria C.G. Juenger b

a Texas Materials Institute, University of Texas at Austin, 1 University Station C2201, Austin, TX 78712, USA
b Department of Civil, Architectural, and Environmental Engineering, University of Texas at Austin, 1 University Station C1748, Austin, TX 78712, USA

A R T I C L E   I N F O

Article history:
Received 19 June 2012
Accepted 8 August 2012

Keywords:
Sulfoaluminate (D)
Expansion (C)
Ettringite (D)

A B S T R A C T

Reply to the discussion of the paper “Understanding expansion in calcium sulfoaluminate-belite cements” by G.L. Valenti, M. Marroccoli, M.L. Pace, A. Telesca.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

We would like to thank Valenti et al. [1] for their interest in calcium sulfoaluminate-belite (CSAB) cements and their comments on the paper by Chen et al. [2]. The issue of expansion from ettringite formation is of critical importance for the dimensional stability of both CSAB cements and portland cements, and it is valuable to gain exposure for this topic through discussion. Valenti et al. [1] have raised concerns about the depth of the literature review on expansion mechanisms in the paper by Chen et al. [2] and have suggested that we have misrepresented the state-of-knowledge in the literature. Since their discussion was primarily focused on interpretation of the literature rather than the experimental data presented by Chen et al. [2], this reply also focuses on existing knowledge about expansion in cementitious systems and how results from the literature were interpreted and reported in the paper by Chen et al. [2]. In addition, Valenti et al. [1] showed data for a particular CSAB cement composition and suggested that the cement behaved differently than the results from Chen et al. [2] would predict. This perceived inconsistency is also addressed here.

2. Effects of CSAB cement chemistry and particle size distribution on expansion

An initial point in the discussion of Valenti et al. [1] was that the relationships between cement composition and particle size and expansion examined by Chen et al. [2] were already well-established in the literature. In fact, results from published literature were discussed thoroughly and critically reviewed by Chen et al. [2] in the introduction of the paper and appropriate and extensive references were provided. Certainly, much valuable research has been published in this area and our work simply builds upon those efforts. What should be made clear about the literature in CSAB cements is that it is difficult to make generalizations from prior work when each published study examined a cement with a different composition, and most papers do not include phase compositions of the cements used, only oxide compositions. Further, in the published studies showing expansion data either: 1) cement phase compositions were not given, making it difficult to correlate composition and expansion [3], or 2) studying dimensional stability was not the primary focus of the research, so multiple variables controlling expansion were not deliberately controlled [4–6]. A systematic and simultaneous study of the effects of four of the major factors (clinker composition, gypsum content, water-to-cement ratio (w/c) and particle size) on expansion using experiments where only one variable was altered at a time had never before been performed, to our knowledge, and was merited in order to further elucidate the interdependencies of the variables controlling expansion.

3. C 3 A Ŝ crystal structure

Another point raised by Valenti et al. [1] is in reference to the crystal structure of the calcium sulfoaluminate phase. Defining the correct crystal structure of cement phases is of critical importance for accurate Rietveld quantitative analysis, as discussed by Álvarez-Pinazo et al. [7] during their recent work using Rietveld quantitative phase analysis on various calcium sulfoaluminate (CSA) cements. Valenti et al. [1] claimed that the crystal structure of C 3 A Ŝ was
defined in the 1960s. While preliminary models for the structure were developed then, there is ongoing research in this area because researchers have been unable to produce a single crystal large enough to perform a single crystal x-ray diffraction experiment that could definitely identify atomic positions and the actual space group [8]. At the current time, it is unclear if C₄A₃S is cubic [8–11] or orthorhombic [12].

There have been questions raised by other researchers about the choice of space groups used in some studies for defining the crystal structure of C₄A₃S. Fischer et al. [13] cast doubt on the orthorhombic space group Pcc2 proposed by Calos et al. [12] because the refinement had large standard deviations, making it difficult to prove deviations from higher symmetry. Likewise, with regard to the cubic space group I23 proposed by Kondo [11], Fischer et al. [13] stated that this space group was identified in error and that the coordinates given conform to the space group I43m.

4. Effects of water-to-cement ratio and porosity

Both Valenti et al. [1] and Chen et al. [2] agree that the w/c of a CSAB paste plays an important role in expansion. Chen et al. [2] referenced the work Beretka et al. [14] (co-authored by Valenti and Marroccoli) who demonstrated this relationship. We also verified the relationship between w/c and expansion experimentally with CSAB cements of differing compositions, which is something that Beretka et al. [14] did not examine. Both Valenti et al. [1] and Chen et al. [2] agree that unstable expansions can result in systems with low w/c (i.e. understoichiometric water contents) because a substantial amount of unhydrated C₄A₃S and CSH₂ remains after the mixing water is consumed, enabling late formation of ettringite from environmental water that permeates the paste. According to Eqs. (1) and (2) [4], the complete hydration reaction of C₄A₃S and CSH₂ requires a w/c of 0.64, and the complete hydration reaction of C₄AF and CSH₂ requires a w/c of 0.56. The stoichiometric water required for the complete reactions of C₄A₃S and C₄AF with calcium sulfates (Eqs. (1)–(3)) for the CSAB cements evaluated by Chen et al. [2] is listed in Table 1. The hydration reaction of C₄S was not taken into account as it remained mostly unhydrated even at later ages [2].

\[ C₄A₃S + 2CSH₂ + 34H → C₃A₃S₄H₁₂ + 2AH₃ \]  
(1)

\[ 3C₄AF + 12CSH₂ + 110H → 4C₆(A·F)₂H₁₂ + 2(A·F)H₁ \]  
(2)

\[ CS + 2H → CSH₂ \]  
(3)

Chen et al. [2] noted that the literature suggests a relationship between pore size distribution and expansion and used w/c as a proxy to indicate porosity of the system. We did not directly test the relationship between pore size distribution and expansion, but took observations from the literature into account when explaining the effects of w/c on expansion. Valenti et al. [1] suggested that the pore size distribution is related to the initial space available, dictating by w/c, and also the “specific volumes of reactants and products,” meaning the degree of hydration of the system. We agree with this statement. For a given cement, at equivalent degree of hydration, lower w/c should result in a denser microstructure with less total porosity [15]. Likewise, for a given cement, at a given w/c, increased degree of hydration should result in a denser microstructure with less total porosity [15]. This point is not in contention. However, since degree of hydration was not explicitly examined by Chen et al. [2], only the influence of w/c on porosity was considered and discussed. We compared samples at the same age, assuming the degree of hydration of the reactive phases was similar, when looking at the effects of w/c on porosity and expansion.

The primary basis for Valenti et al.’s [2] challenge to the relationship between w/c and expansion proposed by Chen et al. [1] comes from their experimental data that do not match our conclusions. As mentioned earlier, Chen et al. [1] hypothesized that a CSAB cement should be expansive if it has an understoichiometric water content because a large amount of ettringite may form after initial hydration when the system is in contact with water from the environment. This hypothesis was partially based on Beretka et al.’s work [14] (co-authored by Valenti and Marroccoli), which showed that two high C₄A₃S (50–55%) and C₆S (25–28%) CSAB cements were dimensionally stable with stoichiometric w/c (0.65–0.7) but expanded and cracked with understoichiometric w/c (0.4) at later-age due to large amount of ettringite formation after the development of a dense microstructure. Valenti et al. [1] proposed a counter example to this point, citing work by Bernardo, Teleca, and Valenti [16], in which a rapid hardening, low porosity CSA cement with more than 50% C₄A₃S and less than 20% calcium sulfate using a 0.5 w/c was shown to be dimensionally stable, in spite of a slightly understoichiometric w/c. However, these specimens were used for drying shrinkage testing, and were, therefore, not exposed to water after the initial hydration period, which explains the lack of expansion.

Valenti et al. [1] used another example of a shrinkage compensating, dimensionally stable system using previously unpublished drying shrinkage results for a mixture of 60% CSA and 40% portland blended cement (0.4 w/c), where the shrinkage-compensating effect was associated with its higher porosity. Again, specimens stored at 50% relative humidity (RH) should not have comparable dimensional changes to those stored in water or 100% RH; samples stored at 50% RH cease hydrating and experience drying shrinkage while samples stored in a wet environment continue hydration. Bernetka et al. [14] also pointed out that the hydration of CSA cements cannot proceed when cured in dry conditions (67% RH); in such conditions the cements continually shrink up to one year (0.39–0.48% shrinkage) regardless of the CSA cement phase composition (6 cements were tested with 15–55% C₄A₃S). Therefore, it cannot be claimed that the results shown by Valenti et al. [1] conflict with those shown by Chen et al. [2] and Beretka et al. [14]. It is inappropriate to compare the dimensional stability of a CSAB cement curing in a wet environment where ettringite is forming through hydration to the normal stability (shrinkage) associated with drying. In addition, CSA cement and CSA-portland blended cement have very different hydration chemistries and could result in very different expansive behaviors.

Finally, Chen et al. [2] did not conclude that CSAB cements with high C₄A₃S and calcium sulfates contents and low w/c will necessarily result in expansive behavior. We demonstrated that expansion and cracking could be eliminated by reducing the CSAB cement particle size distribution, preventing localized expansion caused by the coarser C₄A₃S particles [17,18].

Interestingly, Valenti et al. [1] observed less drying shrinkage in the CSA-portland blended cement compared to the CSA cement alone, which they linked to the CSA-portland cement’s higher total porosity and unimodal narrow pore size distribution (50–90 nm); they claimed that these are a result of expansive ettringite formation. Also the CSA cement had more capillary pores in the 5–50 nm range, while the CSA-portland blend had fewer pores in the 5–50 nm range.

Table 1

<table>
<thead>
<tr>
<th>Clinker</th>
<th>C₄A₃S</th>
<th>C₄AF</th>
<th>C₆S</th>
<th>C₄S</th>
<th>Gypsum required (experimental)</th>
<th>Stoichiometric w/c</th>
</tr>
</thead>
<tbody>
<tr>
<td>HS</td>
<td>65.3%</td>
<td>3.2%</td>
<td>8.9%</td>
<td>22.4%</td>
<td>25%</td>
<td>0.54</td>
</tr>
<tr>
<td>MS</td>
<td>42.0%</td>
<td>6.1%</td>
<td>6.8%</td>
<td>44.9%</td>
<td>15%</td>
<td>0.44</td>
</tr>
<tr>
<td>LS</td>
<td>15.4%</td>
<td>7.2%</td>
<td>6.6%</td>
<td>70.8%</td>
<td>8%</td>
<td>0.25</td>
</tr>
</tbody>
</table>
That the CSA-portland blend experienced lower drying shrinkage is consistent with established concrete knowledge that the smaller capillary pores (5–50 nm) contribute more to drying shrinkage [15].

References