Cement and Concrete Research 39 (2009) 65–68

Contents lists available at ScienceDirect

Cement and Concrete Research

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

Short communication

New method for determination of absorption capacity of internal curing agents

N.A. Johansen [a], M.J. Millard [b], A. Mezencevova [b], V.Y. Garas [b], K.E. Kurtis [b,*]

[a] School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332-0245, USA
[b] School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332-0355, USA

ARTICLE INFO

Article history:
Received 11 June 2008
Received in revised form 8 October 2008
Accepted 10 October 2008

Keywords:
Calorimetry (A)
Cement (D)
Mixture proportioning (A)
Organic materials (D)
Shrinkage (C)

ABSTRACT

Accurate assessment of absorption capacity (k) of internal curing agents is necessary to properly proportion cement-based mixtures and to measure their effectiveness in mitigating autogenous shrinkage. Standard methods for quantifying absorption capacity, such as those for coarse and fine aggregate, are not appropriate for the highly absorptive, finely divided materials often used for internal curing. Here, it is demonstrated that the absorption capacity of internal curing materials may be determined from early age heat evolution data measured through isothermal calorimetry. An example application, using pulp fibers as internal curing agents, is used to demonstrate the utility of the method.

1. Introduction

Highly absorptive materials, such as lightweight aggregate, super-absorbent polymers (SAPs), and wood-derived fibers and powders, are increasingly being investigated for use as internal curing agents in cement-based materials [1–4]. When used appropriately, such materials can reduce or mitigate autogenous shrinkage by providing an adequate internal reservoir of curing water throughout the entire concrete microstructure. With ready desorption of moisture initially held within the internal curing agent to the hydrating cement paste, saturation of the paste can be maintained, thus limiting or avoiding self-desiccation in the paste [1–3,5,6]. However, properly dosing these materials can be particularly challenging, because it is difficult to accurately assess the absorption capacity (k) of such finely divided and highly absorbent materials. Given their relatively high surface areas and propensity for holding capillary water between particles, conventional means for assessing absorption capacity in aggregates (e.g., ASTM C 127 and C 128) are not appropriate. These methods rely on surface moisture testing methods that are more effective with larger, mineral-based aggregates. Furthermore, the standard testing methods are generally performed in water, which may not replicate conditions occurring in the cement-based material. That is, it is probable that the absorption capacity of an internal curing agent will vary when examined in water compared to measurements made in concentrated solutions, such as the pore solution occurring in cement-based materials. Ideally, assessment of an internal curing agent's k should be performed at conditions similar to those in actual concrete.

It is critical that the absorption capacity of an internal curing agent be accurately characterized, as variations will affect dosing of the agent. In addition, inaccuracies can affect interpretations of the internal curing capacity of the material and the influence of internal curing on mitigation of autogenous shrinkage and strength development. For example, if a "lower-than-actual" absorption capacity is used for dosing of the internal curing agent and for mix water adjustments, higher initial strength may result from the resulting actual lower w/c (due to excess mix water absorption), not necessarily from the effects of internal curing [5]. Also, in this case, the autogenous shrinkage measured may be greater than actual, leading to misinterpretations of the agent's ability to provide internal curing.

Therefore, it is desirable to have a method for characterizing the absorption capacity of finely divided materials, such as those used for internal curing, where the assessment of k can occur in cement-based materials (i.e., using true pore solution, rather than water or simulated pore solution) and where absorption is actually quantified (i.e., rather than measuring the results of absorption on structure). Here, a new method is proposed which is based upon isothermal calorimetry. In this method, cement pastes are prepared with slightly varying w/c ratios, and their early heat of hydration data are compared to data of a paste containing an internal curing agent. With knowledge of the initial (or as-received) moisture content (MC) of the internal curing agent and mixture proportions, comparison of the early hydration behavior reveals the amount of water absorbed by the internal curing agent. A step-by-step description of this methodology and an example application of this method are provided herein.

* Corresponding author. School of Civil and Environmental Engineering, Georgia Institute of Technology, 790 Atlantic Dr., Atlanta, GA 30332-0355, USA. Tel.: +1 404 385 0825; fax: +1 404 894 0211.
E-mail address: kkurtis@ce.gatech.edu (K.E. Kurtis).

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doi:10.1016/j.cemconres.2008.10.004

2. Methodology

In this method, it is assumed that the internal curing agents (when MC<k) will absorb water from the mix to equilibrate at their absorption capacity and that this water will be subsequently available for internal curing.[1] It is also assumed that the internal curing agent itself neither accelerates nor slows the rate of hydration. Therefore, the early heat evolution data obtained by isothermal calorimetry for a sample with internal curing, prepared at a given w/c, can be compared to ordinary cement pastes prepared at similar w/cs, to determine the "effective w/c" of the internally cured paste. The effective w/c of the internally cured paste (w/c_E) can then be used with the fiber mixture design to determine how to adjust (Δk) the assumed absorption capacity (k_A) of the internal curing agent for additional executions of the method. These repeated executions of the procedure can allow for the assessment of any effects that the internal curing agent has on early age cement hydration. The steps involved in this process are detailed below.

2.1. Internal curing agent

The moisture content MC (%) of the internal curing agent, which for this example will be pulp fibers, can be determined by placing the as-received material in a 100 °C oven for ~24 h, until the mass remains constant. The MC of the as-received material can be determined from the mass of the oven-dried material (M_{OD}) and the initial mass of the as-received material (M_{AR}):

$$\mathrm{MC}(\%) = \frac{M_{AR} - M_{OD}}{M_{OD}} \times 100 \quad (1)$$

2.2. Mixture design process

The mixture containing the internal curing agent should be designed for a fixed w/c and fixed dry agent-to-cement mass ratio (f/c). Moisture adjustments in the design are based on the difference between the MC of the as-received material and an assumed absorption capacity (k_A), based upon data in the literature or prior experience, of the as-received material. The mass of water proportioned for the mixture (M_W) to maintain the w/c of the mixture can be found by Eq. (2), with M_{CEM} being the mass of cement proportioned for the mixture, and the second term in the equation being the fraction of water added or removed from the mixture by the internal curing agent:

$$M_W = M_{CEM} \times \{w/c - [(MC/100 - k_A) \times f/c]\} \quad (2)$$

The mass of the internal curing agent proportioned (M_F) can then be determined:

$$M_F = M_{CEM} \times f/c \times (1 + \mathrm{MC}/100) \quad (3)$$

A control mixture designed at the same w/c as the internally cured paste will provide hydration curve data for comparative purposes. In addition, pastes will be proportioned at w/c ratios within certain increments above and below that w/c (e.g., +/−0.02 to +/−0.04) to serve as bounding curves. The increments selected can be varied based upon the anticipated absorption capacity of the internal curing agent, the difference between the MC and k_A, and the relative amount of internal curing agent used (f/c).

2.3. Isothermal calorimetry and effective w/c

The internally cured and control pastes should be prepared in triplicate and maintained in an isothermal calorimeter at 25.0+/−1 °C for 24 h, with data recorded at regular intervals. The heat of hydration curve of the internally cured paste can be compared with the hydration curves of the control pastes to interpolate its effective w/c ratio (w/c_E). If the control curves cannot be used to interpolate the w/c_E of the internally cured paste, then additional control pastes with w/cs estimated to be more similar to the curve for the internally cured paste should be made for comparison purposes.

2.4. Absorption capacity determination

With the estimation of w/c_E for the internally cured paste, Eqs.(4) and (5) can then be used to determine the actual k of the material. In Eq. (4), the numerator represents the water entrained by the agent, and the denominator representing the relative dry-material mass.

$$\Delta k = \frac{w/c - w/c_E}{f/c} \quad (4)$$

$$k = k_A + \Delta k \quad (5)$$

3. Example application

Here, the principles outlined above are applied to determine the absorption capacity (k) of pulp fibers, similar to those examined in [1] as an internal curing agent.

3.1. Mixture design

The moisture content of the as-received softwood kraft fiber (Fiber A) was determined to be 108%. Based on data in Mohr et al. [1], the absorption capacity (k_A) of the kraft fiber is assumed to be 1.00.

The fiber sample mixture is designed using 100 g cement, a w/c of 0.30 and an f/c of 0.01 (or 1% oven dry fibers by mass of cement). These values were chosen based upon the understanding that autogenous shrinkage is increasingly significant at w/c values below 0.35 [6] and the limits of workability for pastes containing kraft pulp fibers [1,7]. However, it should be noted that at this w/c and f/c, autogenous shrinkage may be reduced, but not eliminated.

Using Eqs. (2) and (3), the amount of mix water necessary to maintain a w/c of 0.30 is found (29.92 g), and the required mass of as-received fiber for a 1% dry mass fraction paste is determined (2.08 g). The mixture proportions, given with and without moisture adjustments, are detailed in Table 1. In addition, three companion pastes, produced at w/c of 0.26, 0.30, and 0.34 and no internal curing agent, were made for comparison with the fiber sample.

3.2. Sample preparation

Here, pastes were prepared from a commercially available Type I Portland cement (C_3S=49.65%, C_3A=8.29%, C_2S=22.97%, C_4AF=9.04%) and deionized water. For workability, 0.2 mL of superplasticizer (ADVA100, WR Grace) was required in the fiber-containing paste. To avoid effects of variations in superplasticizer dosage and use, this same amount of superplasticizer was used in each of the companion samples.

Table 1
Mixture design for fiber A-cement sample

	Initial design	Design after adjustments
MC (%)	108	108
w/c	0.30	0.30
f/c	0.01	0.01
k_A	1	1
M_{CEM} (g)	100	100
M_W (g)	30	29.92
M_F (g)	2.08	2.08

[1] However, the method is also appropriate if the converse, MC>k, is true. The equations provided here remain applicable, with no changes.

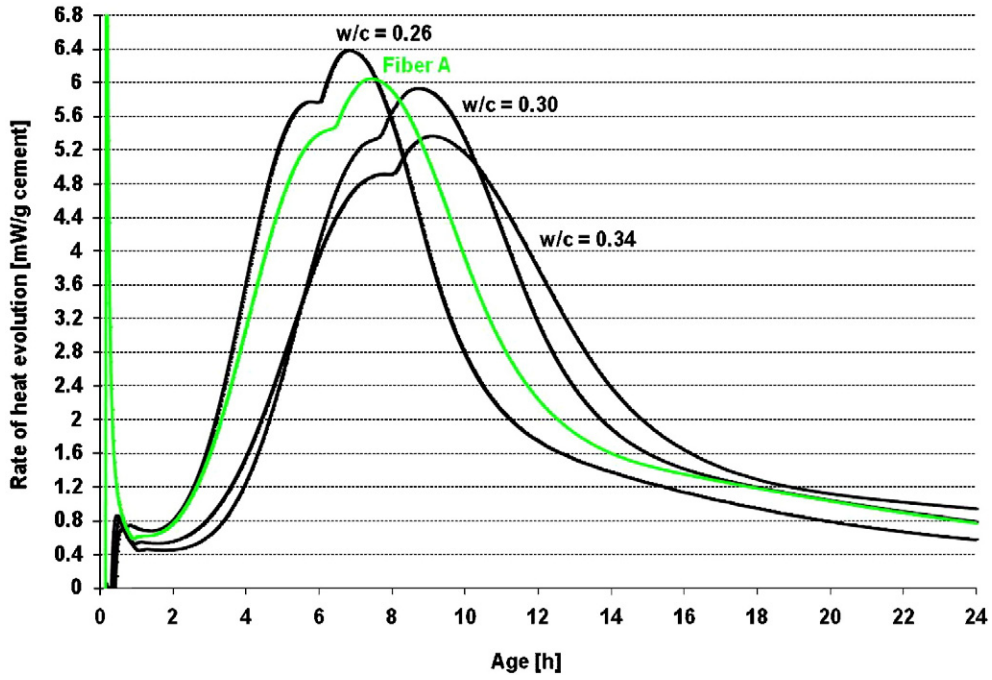

Fig. 1. Normalized heat of hydration with time for ordinary cement pastes (at varying *w*/*c*) and internally cured cement paste containing fiber A.

All tools and materials were kept at 25 °C+/−3 °C for 24 h prior to mixing. The pastes were mixed in a consistent and repeatable way, using a hand mixer. The fibers were used in their as-received moisture state.

Each paste was placed in a pre-tared, temperature-equilibrated, polyethylene ampoule. The ampoules were sealed and weighed. The time spent loading the ampoule with the paste and into the calorimeter was minimized to 2 min to avoid further uncontrolled effects of preparation on the hydration of the cement.

3.3. Isothermal calorimetry and effective w/c ratio

Samples were maintained in an isothermal calorimeter (TAM Air, Thermometric AB, Sweden) at 25.0+/−1 °C for 24 h, with measurements

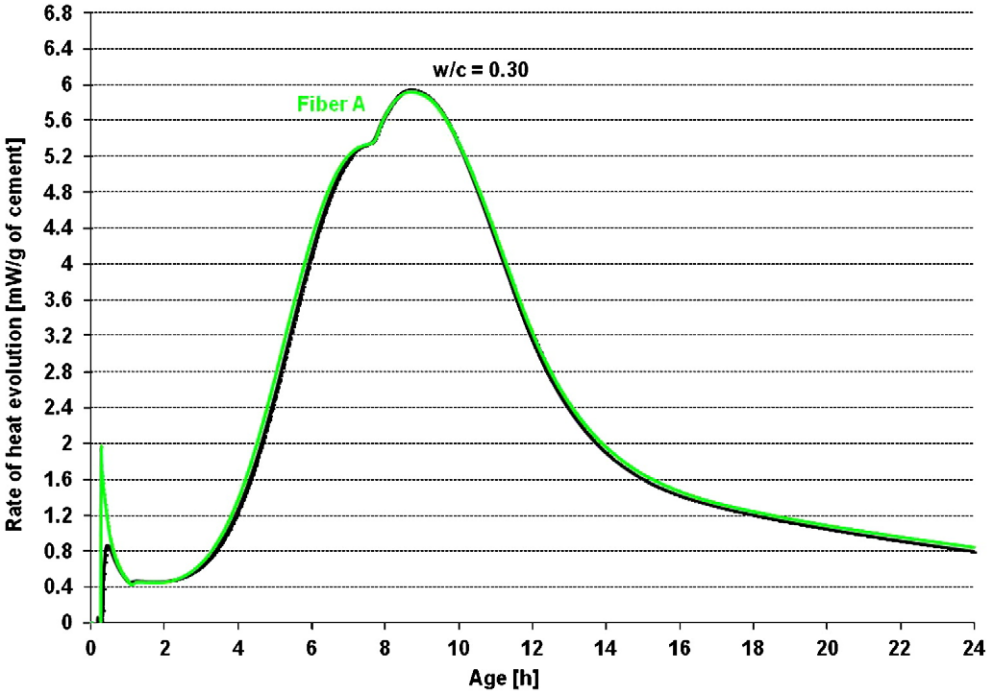

Fig. 2. Normalized heat of hydration with time for fiber A-cement paste, using *k* determined by method, with control paste *w*/*c*=0.30.

recorded every 60 s. The resulting heat of hydration data were normalized per gram of cement and averaged over the triplicates for each sample type.

3.4. Calorimetry data and absorption capacity determination

Fig. 1 shows the rate of heat evolution data for each paste. From inspection of these data, the w/c_E of the Fiber A mixture can be estimated at 0.29. Using Eqs. (4) and (5), the water entrained in the pulp fibers and the absorption capacity of the fibers can be determined:

$$\Delta k = [(0.30-0.29]\ /0.01 = +1.00$$
$$k = 1.00 + 1.00 = 2.00$$

These results show an absorption capacity for Fiber A which is *twice* the value initially assumed based upon data published for a different kraft pulp fiber. This suggests that the absorption capacity for pulp fibers *is* potentially quite variable, validating the premise for this research, and that more precise methods for assessing absorption capacity of internal curing agents are necessary.

3.5. Refinement and validation

Because the absorption capacity measured was different from that assumed for Fiber A, the test should be repeated at $k_A = 2.00$ to validate or potentially refine the results obtained. The resulting hydration curve of the pulp fiber sample at w/c of 0.30 and f/c of 0.01 was found to be very close to the control paste of the same w/c, as shown in Fig. 2. This validates, then, the accuracy of the measured k for this kraft pulp fiber and further iterations are not necessary.

4. Summary of outcomes

A novel method, relying upon heat evolution with time curves generated during isothermal calorimetry, was proposed for the determination of absorption capacity of finely divided materials which may be used for internal curing in cement-based materials. Here, the proposed method showed that the absorption capacity of a kraft pulp fiber, suitable for internal curing, was twice the anticipated value, based upon prior findings in the literature.

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