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On the Relation of Setting and Early-Age Strength Development to Porosity and Hydration in Cement-Based Materials

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Abstract

Previous research has demonstrated a linear relationship between compressive strength (mortar cubes and concrete cylinders) and cumulative heat release normalized per unit volume of (mixing) water for a wide variety of cement-based mixtures at ages of 1 d and beyond. This paper utilizes concurrent ultrasonic reflection and calorimetry measurements to further explore this relationship from the time of specimen casting to 3 d. The ultrasonic measurements permit a continuous evaluation of thickening, setting, and strength development during this time period for comparison with the ongoing chemical reactions, as characterized by isothermal calorimetry measurements. Initially, the ultrasonic strength-heat release relation depends strongly on water-to-cement ratio, as well as admixture additions, with no universal behavior. Still, each individual strength-heat release curve is consistent with a percolation-based view of the cement setting process. However, beyond about 8 h for the systems investigated in the present study, the various strength-heat release curves merge towards a single relationship that broadly characterizes the development of strength as a function of heat released (fractional space filled), demonstrating that mortar and/or concrete strength at early ages can be effectively monitored using either ultrasonic or calorimetry measurements on small paste or mortar specimens.

Keywords: Calorimetry; hydration; percolation; porosity; setting; strength; ultrasonic reflection.

1. Introduction

Historically, concrete has been evaluated principally based on its compressive strength. Extensive and often expensive testing programs, in terms of both manpower and material resources, are commonly implemented to design new concrete mixtures and assure their consistent performance in meeting a specified target strength value. Thus, it is only natural that researchers have long sought alternative ways to evaluate and predict concrete compressive strengths. Over 80 years ago, Lyse published an extensive study conducted at Lehigh University

on the fresh properties and strength of concrete mixtures [1]. Among the conclusions of the paper, Lyse highlights some key observations concerning concrete strength:

> "5. The strength of the concrete mixes increased proportionately with the increase in the cement-water ratio for any brand of cement used and for both ages at test *(7 d and 3 months)*.
>
> 6. The conclusion is reached that the cement is the strength-giving constituent in concrete and that above a minimum number of cement particles necessary to give workability and binding strength to the concrete, the strength of the concrete *(at a given age)* increases in direct proportion to the increase in number of cement particles in a unit *(volume)* of water.
>
> 7. Each brand of cement had its own straight-line relation between the strength and the cement-water ratio of the concrete" (parenthetical additions made by present authors).

The latter conclusion was similarly reached by Bolomey a few years later and came to be known as Bolomey's law [2]. These observations imply that there would also be a one-to-one relationship between strength and water-to-cement ratio (*w/c*), but not a simple linear one (e.g., Abram's law [3]); in fact, *w/c* and its water-to-cementitious materials ratio (*w/cm*) counterpart are still conventionally employed when designing a new concrete mixture to provide a given target strength value, using American Concrete Institute (ACI) [4] or other documented procedures. This paper will further explore relationships between strength development and porosity and hydration in cement pastes, focusing specifically on early age behavior (to 3 d).

2. Theory

2.1 Porosity

The observation that "the strength of the concrete increases in direct proportion to the increase in number of cement particles in a unit of water" could be easily extended to hypothesize that strength development over time would be directly proportional to the volume of hydration products produced per unit volume of mixing water (that ratio being denoted in this paper as F), also equivalent to the fraction of the initial porosity that has been filled by solid hydration products, neglecting any air voids that may be present in the mixture. In 1973, Fagerlund presented such an analysis for the relation between strength and porosity for concrete, described by an equation of the form:

$$\sigma = \sigma_0\left(1 - \frac{P}{P_{cr}}\right) \tag{1}$$

where σ is strength, σ_0 is the (maximum) strength attained at zero porosity, P is porosity, and P_{cr} represents a critical porosity (unique to each set of mixture proportions) above which concrete has no strength [5]. In his derivation, Fagerlund recognized that "a concrete has no strength until a certain degree of hydration is reached" and therefore also presented an accompanying equation for estimating P_{cr} as a function of the water content of the fresh mixture [5]. In the present research, the additional assumption is made that P_{cr} is exactly equal to this initial water content (see Figure 1), neglecting the small amount of hydration (≈ 10 %) commonly required to achieve initial setting.

As illustrated in Figure 1, the quantity $F=(1-P/P_{cr})$ would vary from 0 at the time of initial water-cement contact to a maximum value ≤ 1 when the ultimate degree of hydration is

achieved, due either to complete depletion of the cement, complete depletion of the mixing water, or elimination of the capillary porosity along with depletion of the mixing water (only under saturated curing conditions). In the former two cases, the final value of the fractional space filled would be less than 1, as some capillary porosity would remain in the hydrated system. In these two cases, when additional curing water is not supplied from an external or internal source, some of the initial water-filled porosity will remain as empty pores, due to the chemical shrinkage and self-desiccation that accompanies the cement hydration reactions [6,7]. As illustrated in Figure 1, implicit in this analysis is the additional simplifying assumption that any hydrated system that achieves zero capillary porosity, regardless of the initial ratio of cement to water, will produce the same measured strength. This assumption likely holds only for a limited range of *w/c* or *w/cm*, as very low values for these ratios will likely produce higher strengths, due to the presence of a significant quantity of (stiffer) unhydrated cement particles.

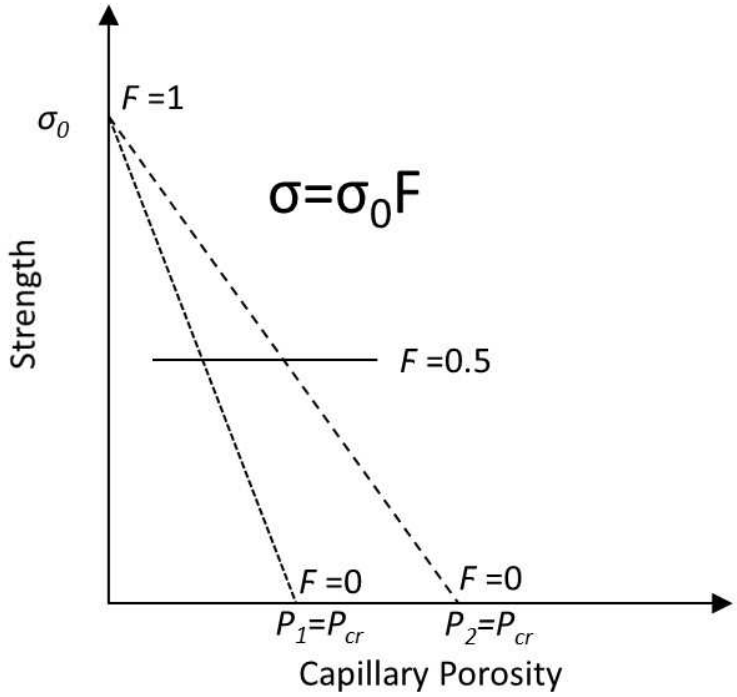

Figure 1. Illustration of hypothesized linear relationship between strength and capillary porosity for two different starting *w/c* (capillary porosities of P_1 and P_2). For the two dashed lines shown, F=1 corresponds to the elimination of capillary porosity in the systems, with an achieved strength of σ_0 in all cases.

The factor $(1-P/P_{cr})$ in equation (1), and its variant, F, used in this paper are similar, but not identical, to the well-known gel-space ratio of Powers and Brownyard [7] that is defined as the ratio of the volume of hydrated cement to that of (the hydrated cement + capillary pores). For the gel-space ratio, the denominator changes with the degree of hydration (as space occupied by hydrated cement was formerly occupied both by porosity and original cement particles), while for the analysis illustrated in Figure 1, the denominator (P_{cr}) is fixed at a constant value, corresponding to the initial mixing water volume (porosity) in the present study. They are also similar to, yet distinct from, another equation that has been successfully utilized in the past to fit

strength vs. capillary porosity data, taking the form $\sigma = \sigma_0 (1 - E \cdot P)$, where E is simply a fitting parameter that is not a specified function of mixture proportions [8,9].

2.2 Heat Release

When one considers that, to first order, the volume of hydration products can be assumed to be proportional to the heat released by the ongoing chemical reactions, the above hypothesis leads to the inference that a plot of measured strength vs. cumulative heat release per unit volume of (initial) water should be a straight line. This hypothesis has been validated for a wide variety of mortar mixtures with *w/cm* less than 0.43 and at ages from 1 d to 28 d, as exemplified by the data sets included in the plot in Figure 2 [10]. Thus, while isothermal calorimetry heat release results are conventionally normalized per gram of cement (cementitious material), normalization per unit volume of water produces the single linear relationship (with some scatter) between strength and heat release shown in Figure 2, consistent with the model outlined in Figure 1.

Relating compressive strength to heat release is distinct from applying a maturity-based method to estimate concrete strengths [11]. Maturity accounts for the time-temperature history of a concrete specimen to compute an equivalent age (based on a user-supplied activation energy) that is then used along with an experimentally measured calibration curve of compressive strength vs. equivalent age to estimate strength. However, maturity concepts could be equally applied to isothermal calorimetry data obtained at different temperatures [12] and plotted to obtain a master heat release vs. equivalent age curve, with Figure 2 essentially providing the subsequently needed (calibrated) relationship between heat release and compressive strength.

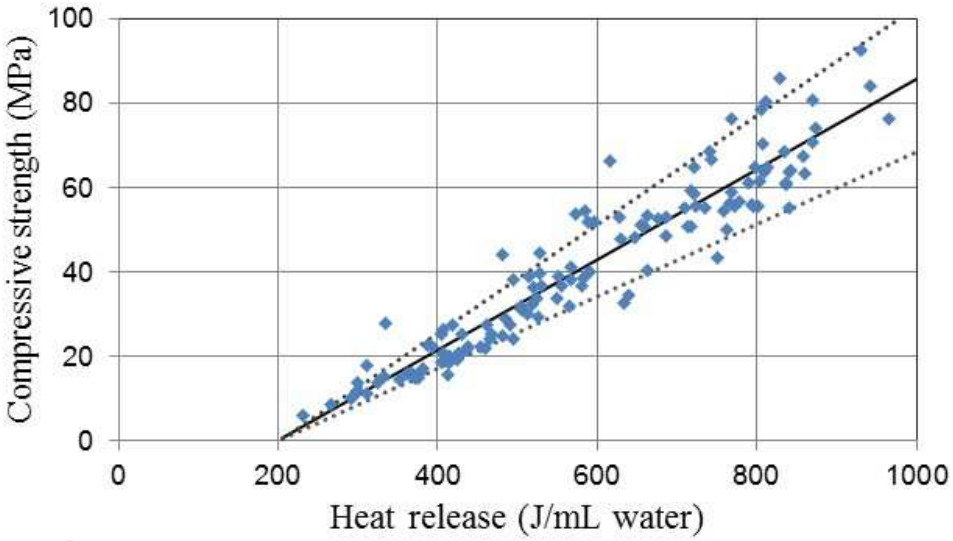

Figure 2. Compressive strength vs. heat release per mL of water for mortars [10]. The solid line indicates the best fit linear relationship (R^2=0.896), while the two dashed lines indicate ± 20 % from the best fit values.

While the data in Figure 2 illustrate a reasonably linear relationship between strength and normalized heat release, it is noted that inherent with this model, there is an offset of a minimum amount of heat release/hydration (about 200 J/mL water) prior to the development of a

measurable cube strength, consistent with Fagerlund's original observations [5]. This leads to the question of how heat release relates to stiffening/hardening during the setting process and whether heat release might be used to predict setting times in addition to predicting strengths. A simple scenario to explore this issue further would be to measure the influence of a change in *w/c*, as it is well known that an increase in *w/c* increases setting times [13]. With this in mind, representative isothermal calorimetry results for heat release rate normalized by either cement mass or water volume are provided in Figure 3 for tests conducted on cement pastes prepared from two different cements in two different labs. Any difference in time of setting is not properly reflected in the heat release rate normalized by mass of cement (nor its integral to obtain heat release), as the five curves for *w/c* ranging from 0.30 to 0.50 basically overlap one another for the first 8 h (which always exceeds the initial setting time). At these early ages, heat release is controlled by the exposed surface area of the cement in the mixtures, as all of them contain sufficient water around the cement particles to satisfy their hydration needs. At intermediate ages, as seen in the plots in Figure 3, heat rate is controlled by the initial water content of the mixture, while at later ages, both cement and water fractions influence the heat release rate [14].

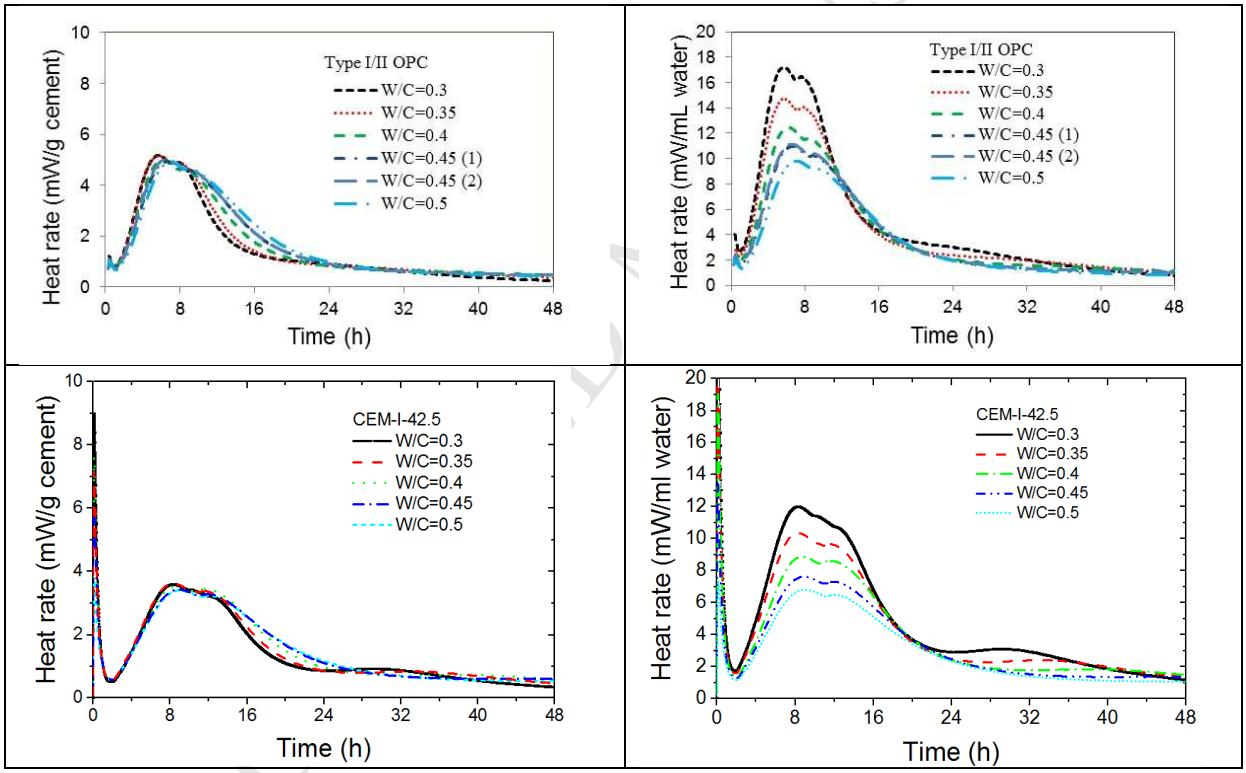

Figure 3. Heat release curves as a function of *w/c* for experiments conducted at NIST (top) and Sika (bottom) expressed on either a per gram of cement (left) or a per volume of water (right) basis. Two replicates (basically overlapping) are shown for the NIST *w/c* = 0.45 pastes to provide some indication of variability. Note that the initial mixing exothermic peak is not captured using the NIST experimental procedure, but is clearly seen in the Sika data that employs insitu mixing.

The distinct nature of the curves on the right side of Figure 3 suggests that normalizing cumulative heat release per unit volume of water might produce a better distinction of setting times than that provided by the conventional normalization per unit mass of cement. For the five

Type I/II OPC pastes with different *w/c* and employing this normalization by unit volume of water, Figure 4 presents the results for cumulative heat release vs. hydration time and also notes their initial setting times measured via Vicat needle penetration per ASTM C191 [15]. A relationship between time of setting and cumulative heat release is evident, but the value of cumulative heat release required to achieve initial setting is not independent of *w/c*, implying that the prediction of times of setting based on calorimetry measurements without additional knowledge of a field mixture's *w/c* (or *w/cm*) could be problematic. A similar difficulty can be encountered when admixtures, such as high range water-reducing agents (HRWRAs), are included in the concrete mixture. Even in cases where the HRWRA has minimal impact on heat rate (kinetics), it may produce a significant delay in time of setting, due to the increased dispersion of the cement particles. This all leads to the subsequent question as to at what age (prior to 1 d) do the strength prediction capabilities of heat release measurements manifest themselves? The present study attempts to answer this question using a combination of continuous ultrasonic and calorimetry measurements.

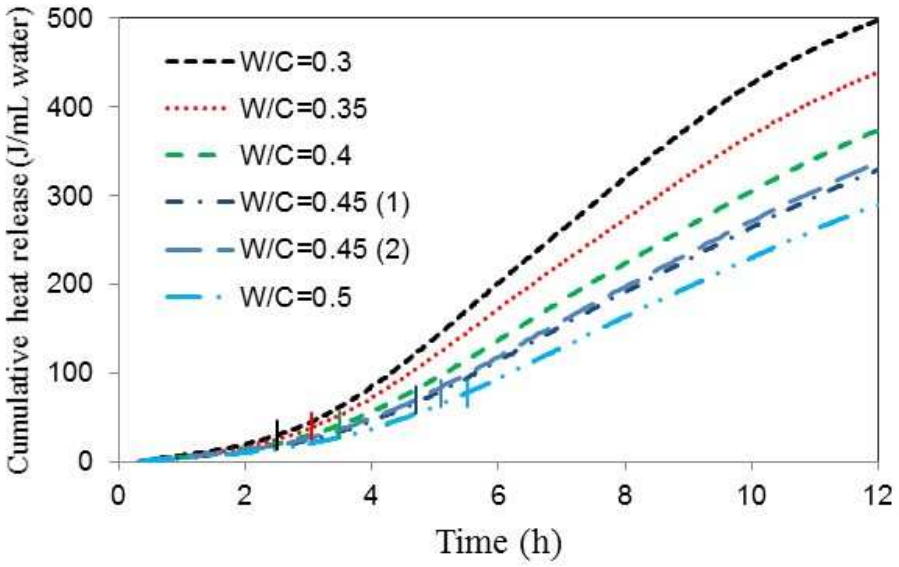

Figure 4. Cumulative heat release per mL (mixing) water vs. time for Type I/II OPC pastes with *w/c* ranging from 0.30 to 0.50. Short solid vertical lines on each curve indicate time of initial set as determined using an automated Vicat apparatus (single laboratory precision of 12 min [15]). Two replicate results are shown for the *w/c* = 0.45 pastes.

2.3 Ultrasonics

In recent years, ultrasonic measurements have been applied to estimate both strength [16,17] and setting times in cement-based materials [18-20], following earlier efforts centered on determining the *w/c* of fresh concrete [21]. In this study, ultrasound spectroscopy is used to follow the evolution of the shear modulus of the hydrating cement paste. The echo-mode is used to follow the time-dependent reflected wave amplitude at the interface between the sample and a Plexiglass surface. In this mode, the transducer acts as both the emitter and the receptor of waves, generated at a frequency of 0.8 MHz. A part of the wave is reflected at the cement paste sample/Plexiglass interface and goes back to the transducer. The other part of the wave goes through the sample and then is reflected at the sample/air interface as illustrated in Figure 5. The

amplitude of the incident wave A_i at the cement paste/Plexiglass interface is equal to the sum of the amplitudes reflected A_r and transmitted A_t at this interface (assuming no dissipation at the interface). The reflection coefficient *r*, which is the ratio of the amplitude of the reflected wave A_r to that of the incident wave A_i, is linked to the acoustic impedances of the two media (Z_1 and Z_2):

$$r = \frac{A_r}{A_i} = \frac{Z_2 - Z_1}{Z_2 + Z_1} \quad (2)$$

The complex shear modulus, G^*, is then obtained with the following equation, in which ρ is the density of the cement paste sample [22]:

$$G^* = \frac{Z_2^2}{\rho} = \frac{Z_1^2}{\rho}\left(\frac{1-r}{1+r}\right)^2 \quad (3)$$

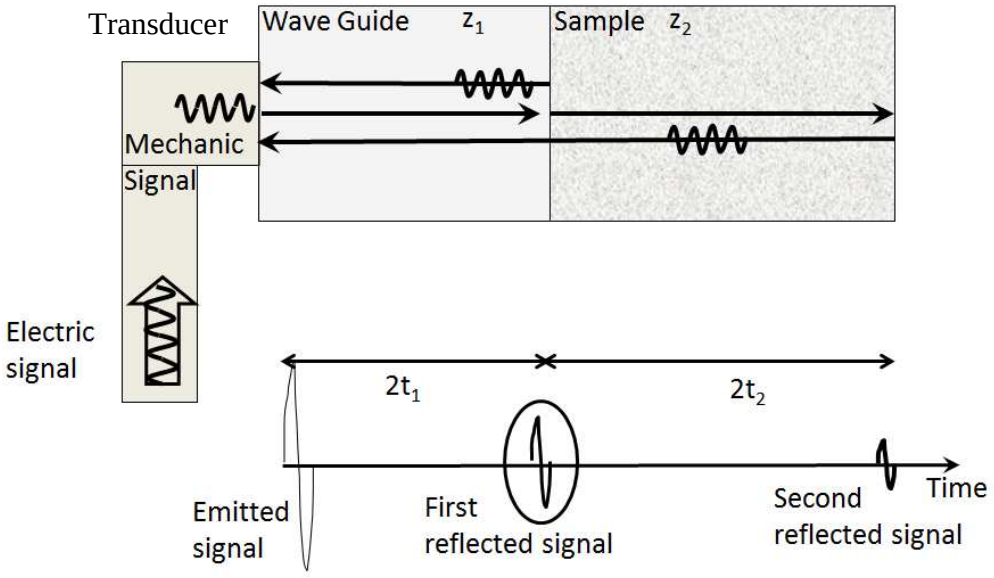

Figure 5. Ultrasonic propagation principle for the measurement of the reflected waves. A transducer is used to convert an electrical to a mechanical signal (left); the generated wave propagates on the wave guide and is partially reflected at the interface with the sample. The second part of the signal is reflected at the interface between the sample and air. The bottom graphic represents the corresponding emitted, first and second reflected signals.

3. Materials and Experimental Procedures

3.1 Materials

Two cements respectively meeting the specifications of CEM I-42.5 and CEM II-42.5 were employed in the present study. Various chemical admixtures were employed in the cement paste mixtures to examine their influence on heat release and ultrasonic measurements. These included a conventional $CaCl_2$ chemical accelerator, a retarder (designated as "P"), and a

"seeding" admixture that provides nucleation sites for calcium silicate hydrate gel (C-S-H) hydration products. Dosages of these admixtures were consistent with current practice.

3.2 Calorimetry Description

Isothermal calorimetry was conducted at 22 °C using a TAMAir[1] device with 8 individual specimen cells. Semi-adiabatic measurements have been conducted with a noncommercial device also containing 8 individual cells. A temperature sensor of type PT 100 B 1/3 is used to record the temperature history of a fresh sample (120 g) that has been poured into a calibrated isolated container. Knowing the thermal transfer coefficient of the container, the quantitative evolution of the heat generated during the chemical reaction can be calculated by considering the temperature rise of the specimen and the heat lost to the environment as:

$$Q(t) = \rho V C_p[T(t) - T_e] + kA\int_0^t [T(t) - T_e)]dt \quad (4)$$

where *Q(t)* is the cumulative heat, T_e the exterior temperature in Kelvin, *T(t)* the temperature of the sample in Kelvin, *A* the area of the contact surface between the sample and the cell, *V* the sample volume, C_p the specific heat capacity of the paste (calculated using values of 0.88 J/(g·K) for the cement and 4.169 J/(g·K) for the water), and *k* the thermal transfer coefficient of the box, determined by monitoring the temperature decay of a heated non-reactive specimen placed in the calorimeter. The technique has a reproducibility of 20 J/g after 24 h.

3.3 Ultrasonic Description

The ultrasonic measurements have been made with a noncommercial instrument. Ultrasonic shear sensors from Panametrics (1 MHz frequency) are used to follow the evolution of the shear wave attenuation as a function of the time [22,23]. An average of three ultrasonic measurements is made for each sample to improve the accuracy. A reproducibility of ± 20 % of the strength values is obtained with the technique. The sample is poured into a measuring cell made of Plexiglass that is 100 mm in diameter and 10 mm high. Measurements were taken every 5 s for at least 48 h.

Ultrasonic data for shear modulus (equation 3) were converted to a strength (in units of MPa) based on the assumption of a constant critical strain, d_0 [24], assuming compressive strength, σ, to be the maximum of the linear stress-strain relation as shown in equation (5):

$$\sigma = E \cdot d_0 \quad (5)$$

To use equation (5), shear modulus *G* from the ultrasonic measurements is converted to Young's modulus, *E*, via Poisson's ratio (assumed to be 0.25 in this study) as:

$$E = 2G(1 + \nu) \quad (6)$$

[1] Certain commercial products are identified in this paper to specify the materials used and procedures employed. In no case does such identification imply endorsement or recommendation by the National Institute of Standards and Technology or Sika Technology AG, nor does it indicate that the products are necessarily the best available for the purpose.

4. Results and Discussion

Figure 6 provides a plot of the time evolution of strength measured via ultrasonic testing and heat release measured via isothermal calorimetry for a cement paste prepared with *w/c*=0.35. The shape of the strength curve is consistent with a percolation-based view of the cement setting process, as bridges of hydration products are built between the cement clinker particles, providing the necessary connections to transform the cement paste from a viscous suspension to a rigid load-bearing solid [25-27]. The initial pseudo-linear portion of the strength curve (Zone A) corresponds to an increase in viscosity of the suspension as connections begin to form and particles "agglomerate" into larger clusters. This is followed by a period of rapid strength gain during and through the initial "setting" of the cement paste (about 2 h to 8 h, denoted by Zone B in Figure 6). Finally, there is a period of slower strength development as the hydration becomes diffusion limited. During this diffusion-limited regime, it is observed in Figure 6 (Zone C) that the cumulative heat release and strength development curves basically overlap one another (when properly scaled), implying that a linear relationship should exist between the two for this time range (8 h and beyond). However, during the solids percolation process within Zone B of Figure 6, there is a more significant change in strength than there is in heat release, implying that a small amount of hydration impacts a much larger change in the strength of the three-dimensional microstructure. Percolation is a critical phenomenon and, like all critical phenomena, a property changes dramatically as a function of an independent variable, in this case volume of hydration products and therefore heat release. This also suggests that there will be less correlation between heat release and setting than there is subsequently between heat release and strength.

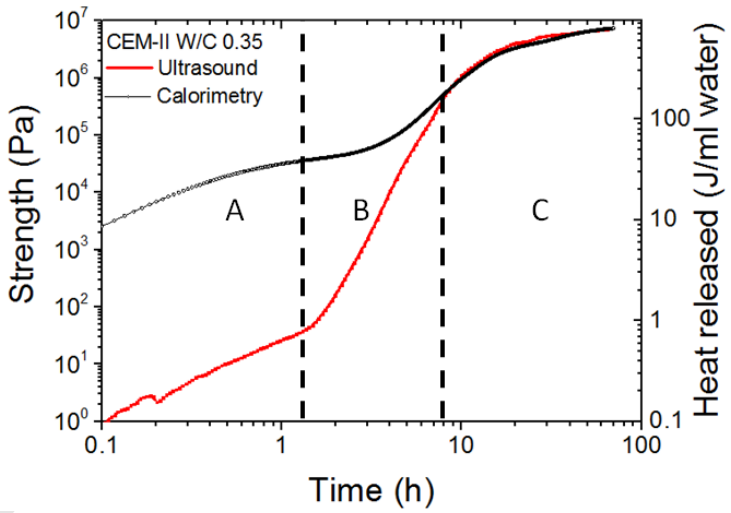

Figure 6. Strength (left) and cumulative heat (right) evolution as a function of time for a cement paste prepared at a *w/c* of 0.35.

For a wider variety of mixtures, Figure 7 provides a plot of measured strength via ultrasonics vs. cumulative heat release, the latter normalized per unit volume of (mixing) water. The divergent behaviors experienced at early ages by the different mixtures are seen to merge into a single universal relation at a strength value of about 10^6 Pa or a cumulative heat release value of about 200 J/mL, the latter value being consistent with the results presented earlier in

Figure 2. These values would correspond approximately to an age on the order of 8 h (see Figure 6 for example), suggesting that onwards from several hours after final setting occurs, heat release measurements could provide the potential to predict early-age strength development with reasonable accuracy. Figure 8 provides the same data on a linear scale to better observe the scatter in the data and the general nature of the linear relationship.

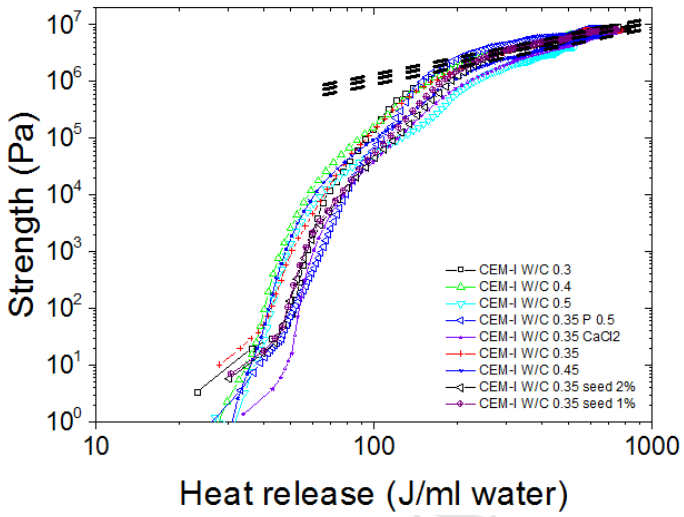

Figure 7. Evolution of cement paste strength as a function of the heat release per volume of water (left). The representations of the strength at the times of initial and final setting are represented by two horizontal lines. The approximately one to one relation between strength and heat release is represented with the 3 dashed lines (two of them indicating ± 20 %).

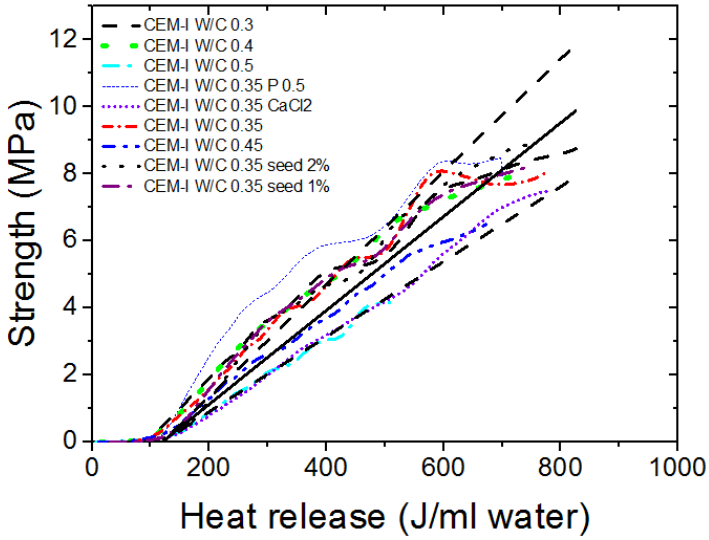

Figure 8. Strength vs. heat release on a linear scale, indicating the linear relationship between these two variables. The approximately one to one relation between strength and heat release are represented with the 3 dashed lines (two of them indicating ± 20 %).

The general insensitivity of the strength-heat release relationship to the presence of chemical admixtures observed in Figure 7 is consistent with the observations of Beaudoin and

MacInnis [28], who remarked that "the volume concentration of hydrate substance and hence porosity appears to be the most important strength parameter, regardless of the presence of admixtures." This dominance of porosity in determining strength would manifest itself as a universal relationship between strength and heat release (per unit volume of water), as shown in Figures 7 and 8.

5. Conclusions

Because porosity is the key parameter regulating strength in cement-based materials, the generally linear relationship between heat release and porosity filled during hydration allows for the development of a linear relationship between strength and cumulative heat release, when the latter is properly normalized per unit volume of water initially present in the mixture. While conventional strength testing (mortar cubes and concrete cylinders) had indicated that this relationship holds for testing ages of 1 d and beyond, continuous ultrasonic measurements have indicated that the relationship is valid from about 8 h (or several hours after final set) onward for the pastes examined in the present study. These results imply that either ultrasonic measurements or calorimetry could be employed to monitor strength development for quality control/assurance purposes.

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References

1) Lyse, I., "Tests on Consistence and Strength of Concrete Having Constant Water Content," *American Society for Testing Materials*, Vol. 32 (60), 629-636, 1932.

2) Bolomey, J., Granulation et Prévision de la Résistance Probable des Bétons, *Travaux*, Vol. 19 (30), 228-232, 1935.

3) Abrams, D.A., "Design of Concrete Mixtures," Bulletin No. 1, Structural Materials Research Laboratory, Lewis Institute, Chicago, 20 pp., 1918.

4) American Concrete Institute, 211.1-91: Standard Practice for Selecting Proportions for Normal, Heavyweight, and Mass Concrete (Reapproved 2009), American Concrete Institute, Farmington Hills, MI, 38 pp., 1991.

5) Fagerlund, G., "Strength and Porosity of Concrete," Proceedings of the International Symposium RILEM/IUPAC 'Pore Structure and Properties of Materials', Prague, 23 pp., Sept. 1973.

6) Powers, T.C., "Absorption of Water by Portland Cement Paste during the Hardening Process," *Industrial and Engineering Chemistry*, Vol. 27 (7), 790-794, 1935.

7) Powers, T.C., and Brownyard, T.L., "Studies of the Physical Properties of Hardened Portland Cement Paste," Bulletin 22, Research Laboratory of Portland Cement Association, Skokie, IL, U.S.A., reprinted from *Journal of the American Concrete Institute* (Proceedings), Vol. 43, pp. 101-132, 249-336, 469-505, 549-602, 669-712, 845-880, 933-992, 1947.

8) Hasselman, D.P.H., "Relation between Effects of Porosity on Strength and on Young's Modulus of Elasticity of Polycrystalline Materials," *Journal of the American Ceramic Society*, Vol. 46 (11), 564-565, 1963.

9) Röβler, M., and Odler, I., "Investigations on the Relationship between Porosity, Structure and Strength of Hydrated Portland Cement Pastes I. Effect of Porosity," *Cement and Concrete Research*, Vol. 15 (2), 320-330, 1985.

10) Bentz, D.P., Barrett, T., De la Varga, I., and Weiss, W.J., "Relating Compressive Strength to Heat Release in Mortars," *Advances in Civil Engineering Materials*, Vol. 1 (1), 14 pp., Sept. 2012.

11) Carino, N.J., "The Maturity Method: Theory and Application," *Cement, Concrete, and Aggregates*, Vol. 6 (2), 61-73, 1984.

12) Bentz, D.P., "Activation Energies of High-Volume Fly Ash Ternary Blends: Hydration and Setting," *Cement and Concrete Composites*, Vol. 53, 214-223, 2014.

13) Bentz, D.P., Peltz, M.A., and Winpigler, J., "Early-Age Properties of Cement-Based Materials: II. Influence of Water-to-Cement Ratio," *ASCE Journal of Materials in Civil Engineering*, Vol. 21 (9), 512-517, 2009.

14) Bentz, D.P., "Influence of Water-to-Cement Ratio on Hydration Kinetics: Simple Models Based on Spatial Considerations," *Cement and Concrete Research*, Vol. 36 (2), 238-244, 2006.

15) ASTM International, ASTM C191-13, Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle, West Conshohocken, PA, 2013.

16) Voigt, T., Akkaya, Y., and Shah, S.P., "Determination of Early Age Mortar and Concrete Strength by Ultrasonic Wave Reflections," *ASCE Journal of Materials in Civil Engineering*, Vol. 15 (3), 247-254, 2003.

17) Voigt, T., Sun, Z., and Shah, S.P., "Comparison of the Ultrasonic Wave Reflection Method and Maturity Method in Evaluating the Compressive Strength," *Cement and Concrete Composites*, Vol. 28 (4), 307-316, 2006.

18) Subramaniam, K.V., Lee, J., and Christensen, B.J., "Monitoring the Setting Behavior of Cementitious Materials Using One-Sided Ultrasonic Measurements," *Cement and Concrete Research*, Vol. 35 (5), 850-857, 2005.

19) Sant, G., Dehadrai, M., Bentz, D., Lura, P., Ferraris, C.F., Bullard, J.W., and Weiss, J., "Detecting the Fluid-to-Solid Transition in Cement Pastes: Comparing Experimental and Numerical Techniques," *Concrete International*, Vol. 31 (6), 53-58, 2009.

20) Robeyst, N., Grosse, C.U., and De Belie N., "Relating Ultrasonic Measurements on Fresh Concrete with Mineral Additions to the Microstructure Development Simulated by Cemhyd3D," *Cement and Concrete Composites*, Vol. 33 (6), 680-693, 2011.

21) Popovics, S., and Popovics, J.S., "Ultrasonic Testing to Determine Water-Cement Ratio for Freshly Mixed Concrete," *Cement, Concrete, and Aggregates*, Vol. 20 (2), 262-268, 1998.

22) Lootens D., Jousset P., Martinie L., Roussel N., Flatt R. "Yield Stress during Setting of Cement Pastes from Penetration Tests" *Cement and Concrete Research*, Vol. 39, 401-408, 2009.

23) Lootens D., Rioas J.L, Flatt R., Blank N. "Device and Method for Determining the Dynamic Elastic Modulus of a Material," US Patent 8,215,172.

24) Oblak, L., Lindlar, B., and Lootens, D., "Continuous Monitoring of Strength Evolution of Shotcrete," Spritzbeton Tagung-2012, Alpbach, Austria, 2012.

25) Jiang, S.P., Mutin, J.C., and Nonat, A., "Studies on Mechanism and Physico-chemical Parameters at the Origin of Cement Setting. I. The Fundamental Processes Involved during the Cement Setting," *Cement and Concrete Research*, Vol. 25 (4), 779-789, 1995.

26) Lei, W.-G., and Struble, L., "Microstructure and Flow Behavior of Fresh Cement Paste," *Journal of the American Ceramic Society*, Vol. 80 (8), 2021-2028, 1997.

27) Bentz, D.P., "Cement Hydration: Building Bridges and Dams at the Microstructure Level," *Materials and Structures*, Vol. 40 (4), 397-404, 2007.

28) Beaudoin, J.J., and MacInnis, C., "The Effect of Admixtures on the Strength-Porosity Relationship of Portland Cement Paste," *Cement and Concrete Research*, Vol. 1 (1), 3-11, 1971.