Relating Compressive Strength to Heat Release in Mortars

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Abstract

Conventionally, isothermal calorimetry and ASTM C186 heat of hydration results are reported on a per mass of cement (powder) basis, with typical units being J/g (cement) for example. Based on the recognition that it is the filling of porosity with hydration products that is chiefly responsible for strength development in cement-based materials, there may be merit in instead reporting these results on a per unit volume of (initial) water basis. This paper examines a database of well over 200 mortar mixtures to investigate the relationship between heat release and mortar cube compressive strength development. For reasonably low water-to-cementitious materials ratios ($w/cm < 0.43$), a single universal straight line relationship with some scatter is obtained. Based on numerous experimental data sets and accompanying theoretical computations, the effects of $w/cm$, sand volume fraction, cement chemical composition, sulfate content, cement fineness, the incorporation of a high range water reducing admixture, and curing conditions on this universal relationship are all considered. Fifty data points from the Cement and Concrete Reference Laboratory (CCRL) proficiency sample program are analyzed to develop a linear relationship between ASTM C109 mortar cube compressive strengths and ASTM C186 heats of hydration at 7 d and 28 d. The application of this relationship for virtual testing is also evaluated. In this case, computer simulations would be employed to predict the heat of hydration vs. time for a particular cement and the developed equations would be employed to convert this heat release to a strength prediction at the age(s) of interest. In general, it appears that these relationships can be used to predict mortar cube compressive strengths based on measured heats of hydration, within about $\pm 10\%$ of the experimentally measured strengths. A preliminary analysis of a single dataset for concretes with and without limestone replacement for cement indicates that the linear relationship between strength and heat release likely holds for concretes as well as mortars.

Keywords: Compressive strength; heat release; hydration; isothermal calorimetry; mortar; virtual testing.
Introduction

Compressive strength is the most commonly used property for characterizing a concrete mixture. Years ago, Powers and Brownyard provided a fundamental basis for understanding compressive strength development in cement-based materials as a function of hydration and starting water-to-cement ratio (w/c), based on a gel-space ratio parameter that quantifies the space-filling capabilities of the cement hydration products [1]. Powers and Brownyard found compressive strength to be generally proportional to their gel-space ratio raised to a power, typically in the range of 2.6 to 3.0, with a pre-factor that depended on cement composition and other factors. In the present paper, the relationship between cumulative heat release (indicative of the cumulative hydration) and compressive strength is explored for a database comprising a wide variety of cement-based mortar specimens. Previously, Zelic et al. have investigated the relationship between degree of hydration as assessed by heat release and compressive strength development in mortars containing various quantities of silica fume [2]. They employed Knudsen’s dispersion models [3] to develop a linear relationship between the hydration ratio defined as $\alpha/(1-\alpha)$, where $\alpha$ represents the degree of hydration of the cement, and the strength ratio defined as $f_c/(f_{\infty}-f_c)$, where $f_c$ is compressive strength and $f_{\infty}$ represents the compressive strength after very long curing. They found that the coefficients for this linear relationship were different for each blended mixture of silica fume and cement, thus requiring separate calibration. More recently, Ioan et al. have demonstrated the successful prediction of 28-d compressive strengths based on early-age heat of hydration obtained from semi-adiabatic calorimetry measurements, with a reported accuracy of $\pm$ 2.5 MPa [4]. In the current study, a more universal relationship between compressive strength and cumulative heat release at early ages is sought based on analysis of a database that contains hundreds of mortar specimens comprising ordinary portland cement mortars, mortars with fly ash replacement for cement, and ternary blends of limestone, fly ash, and cement [5-15].

Data Sources

Compressive strengths and calorimetry data were obtained from a variety of published studies on mortars, and one study on concrete, as indicated in Table 1. These studies were conducted at either the National Institute of Standards and Technology (NIST) or at Purdue University. Generally, mortar cube compressive strengths were obtained on specimens that were cured in limewater, with the exception of references [10] and [11], where sealed curing was employed. Conversely, isothermal calorimetry was generally conducted on small specimens of the same mortar mixtures that were placed in sealed vials. (The influence of curing conditions will be addressed in more detail in the Results and Discussion section.) Typically, isothermal calorimetry data are only collected for 7 d or perhaps 14 d, as beyond these times, the signal-to-noise ratio becomes quite small. For the ASTM C109 [16] mortar cube tests [14,15] at ages of 7 d and 28 d, therefore, the cumulative heat release values were instead obtained from the ASTM C186 Standard Test Method for Heat of Hydration of Hydraulic Cement [17], which measures the heat of solution of hydrated paste (7 d or 28 d) and original cement powder samples. The heat of hydration or cumulative heat release is then obtained by difference. For the mixtures, w/c indicates water-to-cement mass ratio for pastes containing only portland cement and water, w/cm refers to water-to-cementitious materials ratio on a mass basis where cementitious material
includes cement and fly ash, and \( w/p \) refers to water-to-powder mass ratio for mixtures with limestone additions where the powder includes cement, limestone, and fly ash if present.

Table 1. Data sources for cumulative heat release and mortar cube compressive strengths employed in the present analysis.

<table>
<thead>
<tr>
<th>Number of data points</th>
<th>Ages (d)</th>
<th>( w/c, \ w/cm, ) or ( w/p )</th>
<th>Blaine fineness (( m^2/kg ))</th>
<th>( C_3S^A ) (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>1, 3, and 7</td>
<td>0.40</td>
<td>302-613</td>
<td>61-62</td>
<td>[5]</td>
</tr>
<tr>
<td>12</td>
<td>1, 3, and 7</td>
<td>0.325-0.425</td>
<td>380</td>
<td>57.5</td>
<td>[6]</td>
</tr>
<tr>
<td>55</td>
<td>1, 3, and 7</td>
<td>0.35-0.427</td>
<td>( \geq ) 376</td>
<td>57</td>
<td>[7]</td>
</tr>
<tr>
<td>24</td>
<td>1 and 7</td>
<td>0.30-0.42</td>
<td>476</td>
<td>52</td>
<td>[8]</td>
</tr>
<tr>
<td>18</td>
<td>1 and 7</td>
<td>0.30</td>
<td>387,613</td>
<td>61-62</td>
<td>[9]</td>
</tr>
<tr>
<td>40</td>
<td>1, 3, 7, and 14</td>
<td>0.30-0.42</td>
<td>476</td>
<td>52</td>
<td>[10]</td>
</tr>
<tr>
<td>40</td>
<td>1 to 14</td>
<td>0.45</td>
<td>476</td>
<td>52</td>
<td>[11]</td>
</tr>
<tr>
<td>81^b</td>
<td>1, 3, and 7</td>
<td>0.38, 0.42, 0.46</td>
<td>various</td>
<td>42-66</td>
<td>[12]</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>(-0.484)</td>
<td>367</td>
<td>52</td>
<td>[13]</td>
</tr>
<tr>
<td>50</td>
<td>7 and 28</td>
<td>0.484 (0.40)</td>
<td>various</td>
<td>various</td>
<td>[14,15]</td>
</tr>
</tbody>
</table>

^A Cement chemistry notation is used throughout this paper: \( C = \text{CaO}, \ S = \text{SiO}_2, \ A = \text{Al}_2\text{O}_3, \ F = \text{Fe}_2\text{O}_3, \ H = \text{H}_2\text{O} \)

^B Compressive strengths for concrete cylinders, heat release on equivalent mortars

Results and Discussion

Influence of \( w/c \)

Typically, isothermal calorimetry cumulative heat release results are reported on a basis of either grams of cement [17] or grams of cementitious binder, typically in units of \( J/g \). While this provides a convenient indication of the reactivity of the cement (cementitious materials), it may not be the best basis for use in comparison to strength data. For example, Figure 1 shows mortar cube compressive strength plotted vs. cumulative heat release on per gram of cement for a series of ordinary portland cement mortars prepared at four different \( w/c \) ranging from 0.325 to 0.425 [6], with a constant volume fraction of sand. While each \( w/c \) dataset shows a highly linear relationship between strength and cumulative heat release (\( R^2 > 0.99 \) in each of the four cases), they are clearly not all the same. Thinking back to Powers and Brownyard’s original gel-space ratio concept, it is primarily the filling of pore space by hydration products that is responsible for strength development in cement-based materials. Since the initial porosity of a paste or mortar is dependent only on the powder and liquid densities and the starting \( w/c \) (neglecting any air voids), it is perhaps not surprising that the data produces four different lines in Figure 1 when the normalization is performed on a per mass of cement basis.

This suggests that it could be informative to plot the compressive strength vs. the cumulative heat release on a per unit volume (mL) of (initial) water basis instead. Each unit of heat release corresponds to a specific new volume of hydration products that fills in the initially available pore space and should therefore contribute to strength development. With this atypical normalization, the results in Figure 2 are obtained. Now, the four datasets for \( w/c \) in the range of 0.325 to 0.425 overlap one another, with some scatter. These data can be fitted to a line, with
a slope of 0.101 MPa/(J/mL), an intercept of -18.14 MPa, and $R^2=0.974$. The negative intercept implies that some heat release (hydration) must occur prior to the beginning of the development of compressive strength. This initial hydration during setting would establish a network of connected (partially) hydrated cement particles that would provide the framework (scaffold or backbone) for future growth and strength development.

![Figure 1](image1.png)

*Figure 1. Compressive strength (1 d, 3 d, and 7 d) vs. cumulative heat release per gram of cement for mortars with four different w/c [6].*

![Figure 2](image2.png)

*Figure 2. Compressive strength (1 d, 3 d, and 7 d) vs. cumulative heat release per mL of (mix) water for mortars with four different w/c [6]. The solid line shows the best fit for the w/c=0.325 to 0.425 data while the two dashed lines indicate ±10 % from the best fit.*

It has been shown that the setting of cement paste, a physical measurement of the percolation of the solids within the cement paste microstructure, is also dependent on the starting w/c [6,18]. With this in mind, it is perhaps surprising that the four datasets in Figure 2 do in fact
overlap, since one might expect a different intercept for each w/c. Apparently, for this limited range of rather low w/c (0.325 to 0.425), the initial flocculation of the cement particles provides a common or similar framework for strength development, independent of their particle concentration (the volume fractions of cement and water). Water reducers were not used in any of these four mortars [6], so that the initial flocculation of their cement particles should be extensive and quite similar, perhaps resulting in the formation of a single three-dimensional floc. For substantially higher w/c, one might expect that even more heat release would be required to establish this backbone and initiate strength development. A single data point for a w/c=0.484 cement mortar [13], prepared with a similar cement from the same cement plant as that used in reference [6], is included in Figure 2 to show that indeed this is the case. As would be expected, for a given heat release, the w/c=0.484 mortar achieved a lower strength than those exhibited by the four lower w/c mortars. This influence of w/c will be explored in more detail when the w/c=0.484 ASTM C109 mortar cube compressive strength results are examined later in this discussion.

Figure 3 shows the extension of this analysis to over 100 mortar specimens taken from recent literature [5] to [9]. All of these mortars have w/c, w/cm, or w/p within the range of 0.30 to 0.427, with some also containing a high range water reducer. While there is certainly more scatter present in this plot than in Figure 2, the data still cluster around a best fit line with a slope of 0.107 MPa/(J/mL), an intercept of -21.5 MPa, and R²=0.896, quite similar to the parameters determined for the much smaller dataset in Figure 2. The majority of the data in Figure 3 fall within the ± 20 % bounding lines for this linear fit relationship, suggesting that for these mortars, their compressive strength could be generally predicted to this level of accuracy via measurement of their cumulative heat release using isothermal calorimetry.

![Figure 3](image-url)  
*Figure 3. Compressive strength vs. heat release per mL of water for mortars from references [5] to [9]. The solid line indicates the best fit linear relationship, with the two dashed lines indicating ± 20 % from the best fit values.*
Influence of Cement Composition

The cements included in Table 1 span a fairly wide range of chemical compositions, with estimated C₃S contents ranging from 52 % to 62 % for those used to prepare mortars. Since each of the four primary phases of the cement powder (alite, belite, aluminate, and ferrite, here estimated as C₃S, C₂S, C₃A, and C₄AF) releases a different amount of heat during its hydration with water (and gypsum in the case of the aluminates) [19], it is somewhat surprising that the data cluster around a single line in Figure 3. However, a more detailed analysis of the relationship between the heat release of a given phase and its porosity-filling capability helps explain why this might be so. Relevant parameters for this analysis are included in Table 2 and Table 3 [19]. Other than the value for C₃S hydration, the computed values for the amount of heat release per unit volume of filled porosity are all on the order of 700 J/mL ± 5 %. This would suggest that as long as the C₃S contents of two cements do not vary over too large a range, their heat release per unit volume of filled porosity would be similar. Specifically, for the range of 52 % to 62 % represented by the mortar data in Figure 3, the different cements all fall basically on a single strength-heat release relationship line. A 10 % absolute change in C₃S (from 52 % to 62 % for example), would shift the heat release value for the cement by about 80 J/mL (≈0.1*(1500-700)), which would cover a substantial portion of the data scatter in Figure 3.

Table 2. Heat release and space-filling capacities of the four major cement clinker phases [19].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Heat of hydration (J/g phase)</th>
<th>Assumed reaction products per one mole of phase (moles)</th>
<th>Molar mass of phase (g/mol)</th>
<th>Computed heat per unit filled volume (J/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>517</td>
<td>1 C₁₇SH₄, 1.3 CH</td>
<td>227.9</td>
<td>1475</td>
</tr>
<tr>
<td>C₂S</td>
<td>262</td>
<td>1 C₁₇SH₄, 0.3 CH</td>
<td>170.6</td>
<td>678</td>
</tr>
<tr>
<td>C₃A</td>
<td>1144^A</td>
<td>1 Ettringite</td>
<td>270.0</td>
<td>730</td>
</tr>
<tr>
<td>C₄AF</td>
<td>725^A</td>
<td>1 Ettringite, 1 CH, 1 FH₃</td>
<td>477.4</td>
<td>710</td>
</tr>
</tbody>
</table>

^A Assuming reaction with sufficient (3 moles of) gypsum to form ettringite.

Table 3. Estimated molar volumes of cementitious phases employed in calculations [19].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Molar volume (cm³/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>71</td>
</tr>
<tr>
<td>C₂S</td>
<td>52</td>
</tr>
<tr>
<td>C₃A</td>
<td>89.1</td>
</tr>
<tr>
<td>C₄AF</td>
<td>128</td>
</tr>
<tr>
<td>Gypsum</td>
<td>74.2</td>
</tr>
<tr>
<td>CH</td>
<td>33</td>
</tr>
<tr>
<td>C₁₇SH₄</td>
<td>108</td>
</tr>
<tr>
<td>Ettringite</td>
<td>735</td>
</tr>
<tr>
<td>FH₃</td>
<td>69.8</td>
</tr>
</tbody>
</table>

Influence of Sulfate Content

The role of sulfate (SO₃) during early-age hydration and development of hardened properties has been a focus of study during the major part of the 20th century [20]. According to Lerch, SO₃ significantly influences the cement hydration affecting the early-age properties (i.e.
strength, shrinkage, etc). A recent Purdue University study examined the performance of mortar mixtures prepared with a wide range of SO\textsubscript{3} contents and cured under sealed conditions [11]. Some of the mortars were also prepared with a large part of the cement being replaced with fly ash, yielding what is called High Volume Fly Ash (HVFA) mixtures. Two of the properties measured in that study were the heat of hydration and the compressive strengths of mortar cubes. Figure 4 shows the strength vs. heat release results of that study and also includes the data points shown in Figure 3 of this paper for comparison purposes. Despite the large difference in SO\textsubscript{3} contents and the different systems used (ordinary portland cement vs. HVFA blended systems), the results show a very good correlation between strength and heat release (dashed line, \(R^2 = 0.949\)). However, these data points don’t fall within the limits assessed in Figure 3, instead lying below this region. This can be attributed to the fact that these mortars had a w/c or w/cm by mass of 0.45 [11], therefore the w/c effect explained in detail earlier would apply to some extent in this case as well. Additionally, these mortars with varying sulfate contents were cured under sealed conditions, contrary to the soaked conditions used for all of the data in Figure 3. This difference in curing conditions will be discussed further later in this paper. In any case, the SO\textsubscript{3} content doesn’t seem to have a measurable effect on this relationship (at least within the range of SO\textsubscript{3} studied [11]).

![Figure 4](image)

**Figure 4.** Compressive strength vs. heat release per mL of water for mortars prepared with various sulfate contents and cured under sealed conditions [11]. The dashed line indicates the best fit linear relationship with \(R^2=0.949\).

*Influence of Cement Fineness*

Reference [5] provides a systematic variation of cement fineness for a set of cements all produced from the same clinker, with each being separately optimized for sulfate content. Figure 5 shows a plot of compressive strength vs. heat release for these data. The data still cluster around the best fit line from Figure 3, but the finest cement (Blaine fineness of 613 m\textsuperscript{2}/kg) is consistently above this line, while the coarsest cement (Blaine fineness of 302 m\textsuperscript{2}/kg) is consistently below it. Cements of intermediate fineness basically fall on the best fit line. Coarser cements will generally produce larger interparticle spaces within the initial
arrangement of cement particles in water [21]. During hydration, these pores may persist as being larger than their counterparts in an equivalent paste prepared with a higher fineness cement, leading to larger flaw sizes and concurrently reduced strengths for an equivalent amount of cement hydration (heat release) [5].

![Graph showing compressive strength vs. heat release per mL of water for mortars prepared with various fineness cements](image)

**Figure 5.** Compressive strength vs. heat release per mL of water for mortars prepared with various fineness cements, as indicated by the median particle diameter of each provided in the legend [5]. Fit to all data line is taken from Figure 3.

**Influence of High Range Water Reducing Admixture**

Because a high range water reducing admixture (HRWRA) influences the initial flocculation of the cement particles, one would conjecture that it could also influence the compressive strength - heat release relationship, particularly the intercept of the best fit line. By dispersing the cement particles and generally increasing their nearest neighbor interparticle distances, it would seem plausible that an increase in HRWRA would shift the relationship to the right, requiring increased heat release to make the initial connections between cement particles and to ultimately achieve an equivalent strength. Conversely, this dispersion of particle will also likely reduce the maximum water-filled pore “size” and could therefore lead to increases in strength at a fixed cumulative heat release value. Unfortunately, of the studies examined here, the HRWRA dosage was included as an independent variable only as a part of the one presented in reference [8]. Amongst the 12 mixtures prepared in that study, two mortars were examined with HRWRA dosages of 0.3 % and 0.8 % by mass of cementitious materials (cement and fly ash), but were otherwise equivalent. All of the data from that study are included in Figure 6, with the two HRWRA-variable mixtures denoted by their own symbols. While it is granted that this is a very limited examination of the influence of HRWRA on the strength – heat release relationship, it does suggest that the points with a higher dosage of HRWRA may be shifted to the right relative to those with the lower dosage, consistent with the hypothesized increase in nearest neighbor interparticle distances. This is a topic that should be examined further as new studies are conducted in which the HRWRA dosage is an independent variable.
Influence of Sand Volume Fraction

For the various published studies included in Figure 3, the volume fraction of the silica sand was always approximately 0.55. It would be expected that sand volume fraction (and mineralogy) might have an influence on the strength–heat release relationship. An ongoing study at NIST [22] has included examination of mortars with 3 different w/cm, each prepared with a different volume fraction of sand. Specifically, the three w/cm with their corresponding sand volume fractions are 0.40 with 0.478, 0.35 with 0.494, and 0.30 with 0.513, respectively. As shown in Figure 7 and considering that w/cm is varying concurrently with sand volume fraction, for sand volume fractions between 0.48 and 0.55, its influence on the strength–heat release relationship appears to be small, as the new data fall within the ±20 % bands established for the composite data set in Figure 3. The type of sand (mineralogy) could potentially influence the strength-heat release relationship as well, but in all of the studies presented in this paper, silica sands were employed.

Influence of Curing Conditions (Soaked vs. Sealed)

Curing conditions are usually expected to have an influence on strength development. In a recent study [10], a large data set was generated for mortars with w/cm from 0.30 to 0.427, but cured under sealed conditions. Figure 8 includes these new data points along with those shown in Figure 3, dividing them into two groups based on curing conditions: soaked and sealed. It can be observed that there is a general trend of the soaked mixtures to lie above the sealed ones, particularly at later ages (greater heat release values). However, both still generally remain within the region delimited by the dashed lines (± 20 % from the best fit values for the data in Figure 3). The effect at later ages is likely due to the fact that in sealed conditions, larger empty pores are formed during self-desiccation and remain during subsequent hydration, reducing the measured strength values (the large empty pores can be viewed as “flaws”). Under soaked conditions, these pores will not empty and their size will be subsequently reduced as the hydration continues, since hydration products will form in all water-filled spaces. However the
difference between soaked and sealed conditions in the strength values is not extreme (15% lower strength values at later ages in the latter case).

Figure 7. Compressive strength vs. heat release per mL of water with data from Figure 3 and data for mortars prepared with various volume fractions of sand.

Figure 8. Compressive strength vs. heat release per mL of water for specimens cured under sealed conditions [10], in comparison to data from Figure 3 (soaked).

Predictions for ASTM C109 Compressive Strength Testing

Cements are commonly evaluated for strength development utilizing the ASTM C109 standard test method [16] for mortar cubes. While this test has specified both constant flow and constant w/c conditions for testing over the years, in recent years, it recommends that Portland cement mixtures be prepared with a prescriptive mixture of 500 g of cement, 1375 g of sand, and
242 g of water, for a batch size of 6 cubes. This provides a mixture with $w/c = 0.484$. Conversely, the ASTM C186 standard test method for heat of hydration [17] is based on a cement paste prepared with 150 g of cement and 60 g of water, for a $w/c = 0.40$ (equivalent to 0.40 mL of water per g of cement). Thus, relating the ASTM C109 compressive strengths to the ASTM C186 heat releases to examine a possible strength–heat release relationship is confounded by the rather different $w/c$ employed in the two tests. While it is well established that compressive strength is a strong function of $w/c$ (and this is usually the basis for designing concrete to a desired strength value), differential and cumulative heat release are much less sensitive to $w/c$ [6,23]. It is also known that at later ages, isothermal calorimetry specimens prepared at low $w/c$ (e.g., 0.30) will release less heat per gram of cement than an equivalent $w/c = 0.40$ paste, due to self-desiccation and space limitations reducing the longer term hydration rates [6,10]. But, for pastes with $w/c$ above 0.40, these effects are typically much less significant and the heat release per gram of cement remains fairly constant as $w/c$ increases. As a first approximation, this implies that the measured heat release in the ASTM C186 test could be converted to an equivalent value to predict strength development in an ASTM C109 test simply by dividing the measured value (in J/g) by the $w/c$, 0.484, of the latter test. As will be demonstrated in the plots to follow, in fact, when this approach is employed, quite reasonable predictions are obtained.

Figure 9 provides a plot of mortar cube compressive strength vs. heat release for twenty different Type I/II cements evaluated in recent years in the CRL proficiency testing program [14], where the heat release has been converted from a mass basis to a volume basis using the $w/c = 0.484$ of the compressive strength testing specimens. Also included in the plot are two data sets from a recent study [13] investigating the ASTM C311 strength activity index of pozzolans [24], where both the compressive strength and isothermal calorimetry measurements were performed on the same mortar mixtures. Here, the mixtures prepared following a constant volumetric proportioning paradigm are seen to fall on the same straight line as the C109 data. Conversely, those prepared using the current constant flow but variable volumetric proportions protocol (indicated by the squares in Figure 9), and with $w/cm$ therefore varying from 0.44 to 0.56 [13], exhibit a significant deviation from the straight line relationship.

Nearly all of the C109 strength data points in Figure 9 fall within the 10 % bounding lines based on the conducted linear regression of C109 strength vs. C186 heat release, implying that in general, compressive strengths could be predicted with this level of accuracy based on the C186-based measurements of heat release. An alternate approach would be to attempt to predict the 28 d strength based on a measured 7 d strength and the measured heat data at both 7 d and 28 d. For the C109 data in Figure 7, the average slope between 7 d and 28 d strength and heat data is determined to be 0.1179 MPa/(J/mL). This would mean that the following equation could be used to predict 28-d compressive strength:

$$\sigma_{pred}(28d) = \sigma(7d) + 0.1179(heat(28d) - heat(7d))$$

(1)

where $\sigma$ represents compressive strength. Using this average value, Figure 10 provides a plot of the predicted 28 d strengths vs. their measured counterparts; on average, the predicted values are within 4.4 % of the measured ones. All but one of the predicted values fall within the ± 8 % bands shown in Figure 10. This prediction accuracy would also be in line with the ± 2.5 MPa
reported previously in the study of Ioan et al. [4], where semi-adiabatic calorimetry was employed.

![Graph](image)

**Figure 9.** Compressive strength vs. equivalent heat release per mL of water for a \( w/c = 0.484 \) paste for data obtained from CCRL proficiency sample testing program [14]. The solid line indicates the best fit relationship (slope = 0.0984, intercept = (-34.3), \( R^2 = 0.829 \)) just for the CCRL 159-180 data set. The two dashed lines indicate ± 10% from the best fit values.

It is interesting to note that the magnitude of the slope for the data in Figure 9, 0.0984 is not that different from the slope magnitude in Figure 3 of 0.107, while their corresponding intercepts are significantly different. This implies that while the amount of hydration necessary to initiate strength development is a strong function of \( w/c \) (or equivalently initial water volume fraction) [6], once strength development begins, the space-filling process is quite similar over the range of \( w/c \) presented in this study. This reflects the same arguments as those of Powers and Brownyard in developing their gel-space ratio approach for predicting compressive strength [1].

*Potential for Virtual Testing Predictions of 28 d Compressive Strengths*

It has been previously demonstrated that virtual testing can be applied to predicting the cumulative heat release of hydrating portland cements [15]. In that study, a microstructural model was calibrated using 24 h measurements of chemical shrinkage and then applied to successfully predicting 7 d and 28 d (ASTM C186) cumulative heat releases. For five cements from the CCRL proficiency sample program (see Table 4), these predicted heat release values were for the most part within a range encompassed by their corresponding experimental values ± two of their measured standard deviations. Based on the relationships established in the present study, namely equation (1), these predictions of heat release can be extended to predictions of mortar cube compressive strength. Table 4 provides a comparison of 28 d cube strength predictions, based on measured 7 d strengths and either measured or simulated cumulative heat releases at 7 d and 28 d. For the five cements investigated, the average prediction error is 4.3%
when equation (1) is applied using the measured heat release values, quite similar to the 4.4 % determined for the data in Figure 10. When virtual testing is employed to provide the heat release values, this average error is increased to 9 %, suggesting that the experimental heat release values should be employed when available, but that the virtual testing may provide a reasonable estimate for compressive strength when the experimental heat release data are not available. If, instead, the regression equation determined for the data in Figure 9 is employed for the strength predictions, the average prediction errors when using the measured or virtual 28 d cumulative heat release values are 9 % and 11.6 %, respectively. As one might expect, this indicates that having the 7 d strength data available improves the ability for predicting the 28 d strength based on heat release measurements.

Figure 10. Predicted 28 d mortar cube compressive strength vs. measured strength for 20 CCRL-tested mortars. The solid line indicates a 1:1 relationship, while the two dashed lines indicate a variation of ± 8 % from this 1:1 relationship.

Table 4. Virtual Testing Predictions for 28 d Compressive Strengths

<table>
<thead>
<tr>
<th>CCRL Cement ID</th>
<th>Measured heat releases (J/g cement)</th>
<th>CEMHYD3D predicted heat releases [15] (J/g cement)</th>
<th>Measured strengths (MPa)</th>
<th>Predicted 28-d strength based on equation (1) and measured values (MPa) (Difference from measured %)</th>
<th>Predicted 28-d strength based on equation (1) and CEMHYD3D (MPa) (Difference from measured %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>7 d-310.9 28 d-368.6</td>
<td>7 d-305.3 28 d-346.3</td>
<td>7 d-30.7 28 d-43.8</td>
<td>44.7 (2.1 %)</td>
<td>40.6 (7.2 %)</td>
</tr>
<tr>
<td>116</td>
<td>7 d-359.8 28 d-402.1</td>
<td>7 d-339.6 28 d-383.0</td>
<td>7 d-33.9 28 d-43.8</td>
<td>44.2 (1.0 %)</td>
<td>44.5 (1.6 %)</td>
</tr>
<tr>
<td>135</td>
<td>7 d-326.4 28 d-360.2</td>
<td>7 d-327.4 28 d-375.0</td>
<td>7 d-31.7 28 d-40.6</td>
<td>39.9 (1.6 %)</td>
<td>43.3 (6.5 %)</td>
</tr>
<tr>
<td>141</td>
<td>7 d-351.1 28 d-380.7</td>
<td>7 d-344.2 28 d-399.6</td>
<td>7 d-32.6 28 d-38.3</td>
<td>39.8 (4.0 %)</td>
<td>46.1 (20.3 %)</td>
</tr>
<tr>
<td>152</td>
<td>7 d-362.8 28 d-415.0</td>
<td>7 d-372.3 28 d-417.3</td>
<td>7 d-37.1 28 d-44.1</td>
<td>49.8 (12.9 %)</td>
<td>48.1 (8.9 %)</td>
</tr>
</tbody>
</table>
It has been well documented that finely ground limestone particles simultaneously dilute the cement volume fraction, act as nucleation sites, and influence the particle packing when included in cementitious systems [25]. The net influence of these mechanisms on the hydration, and subsequently strength development, depends on the nature of the limestone replacement (blended vs. interground) and the level of replacement (i.e. dilution). The results presented in Figure 11 from a recent study by Barrett et al. [12] compare three interground portland limestone cement (PLC) concretes and two blended limestone cement concretes with their ordinary portland cement (OPC) concrete references. The plotted data encompass w/p of 0.38, 0.42, and 0.46 by mass, with limestone replacement levels of 10% to 15% by mass. The compressive strengths of 100 mm x 200 mm concrete cylinders cured under sealed conditions were measured at ages of 1 d, 3 d, and 7 d, while the heat evolution was measured on their mortar counterparts via isothermal calorimetry for 7 d. The results of the study indicate that the replacement of cement with limestone will reduce the amount of necessary hydration before the onset of strength gain, shifting the x-axis intercept to the left towards zero in Figure 11. One potential reason for this is that the cement particles in the interground systems are coarser (than the softer limestone) and less numerous, so that fewer linkages may need to be established between particles during the setting process [18]. This data set provides one concrete example of the ability of the proposed approach to capture the (linear) relationship between compressive strength and heat release in concretes, as opposed to only being applicable for mortars.

![Figure 11. Compressive strength of concrete cylinders vs. heat release per mL of water for mortars from reference [12]. The bold solid line indicates the best fit linear relationship ($R^2 = 0.77$) for the OPC concretes, with the two dotted lines indicating ± 20% from the best fit values. The dashed line represents the best fit for the limestone replacements ($R^2 = 0.76$). The thin solid line represents the best fit determined for the mortar data in Figure 3.](image-url)
Conclusions

The presented results indicate a linear relationship between compressive strength and cumulative heat release when the latter is determined on a per unit volume of initial water basis. While the straight line relation depends on the starting w/cm, for the data investigated in this study for mortars, for w/cm < 0.43, a single line can be used to characterize all of the data. The relationship for mortars is relatively robust, with variability in sulfate content, cement composition, cement fineness, or sand volume fraction, or replacement of cement by fly ash or limestone having only minimal impacts. Sealed curing vs. soaking was observed to have a significant influence on the strength-heat release relationship, particularly for later age specimens. The potential for using ASTM C186 cement paste heat release results to predict the compressive strengths provided by ASTM C109 mortar cube testing has been demonstrated. As an extension of this, virtual testing could be employed to predict both heat release and compressive strength results at 7 d and 28 d. Predictions of mortar cube compressive strength based on isothermal calorimetry heat release are generally within ± 10 % of the measured strength values. Analysis of one dataset for concretes with and without limestone replacements for cement has indicated that the linear relationship between strength and cumulative heat release per unit volume of water is applicable to concretes as well as mortars.

References

11) De la Varga, I., Increased Use of Fly Ash in Concrete Structures, Ph.D. Thesis, Purdue University, 2013.
14) CCRL Proficiency Sample Reports, available at [http://www.ccrl.us/Psp/Reports.htm](http://www.ccrl.us/Psp/Reports.htm) (access verified Sept. 8, 2011).
15) Bentz, D.P., Verification, Validation, and Variability of Virtual Standards, 12th International Congress on the Chemistry of Cement, Montreal, 2007, CD-RoM.