EVALUATING THE EARLY AGE PERFORMANCE OF PORTLAND CEMENT UNDER DIFFERING HYDRATION CONDITIONS

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Abstract
The objective of this work was to examine the hydration performance of Portland cement with variations in Tricalcium Silicate and Tricalcium Aluminate proportions. The performance and durability of Portland cement is affected by its particle size, chemistry, morphology, water availability, thermodynamic reaction rates, and age at which the materials are tested. Portland cement has many phases that all react simultaneously depending on many different factors. How the different phases react while part of the entire system, including how the reactions affect those of other components in the system, was investigated in order to determine how true cement can be expected to behave during hydration. Laboratory research focused on the establishment of early age hydration and formation of the microstructure; techniques for characterizing the hydration and formation of microstructure; effects of time dependent phenomena and aging on microstructure as it relates to durability; and the microstructure based durability index as it relates to strength, shrinkage, and heat production. The goal of this research was to provide the basis for a predictive model capable of predicting the phase composition of a hydrated Portland cement under specified conditions.

Keywords
Portland cement, particle size, activation energy, length change, morphology

1. INTRODUCTION

Current standards and test methods for Portland cement\(^1\) do not take into consideration how a cement will perform with respect to cracking due to the amount of heat that will be produced, activation energy from massive concrete elements, or shrinkage. Currently, there is a movement by the Portland cement concrete industry\(^2\) to improve standards and test methods in order to accept materials based on performance. However, the current lack of performance criteria and test methods means that the performance of the Portland cement concrete cannot be predicted. This study was designed to determine which test methods would be needed for
evaluating the performance of Portland cement with respect to the amount of heat produced, and the effects of cement grind, activation energy, and length change.

2. LITERATURE REVIEW

An extensive literature review was undertaken to determine the effects of particle size in Portland cement, the effects of Portland cement strength gain on massive concrete elements, and the activation energy and length change of cement pastes. This literature review was conducted to analyze the major performance issues of cement pastes to act as the basis for the development of a performance based specification for Portland cements. Due to space limitations, the complete literature review can be found elsewhere.

3. CHEMICAL, MORPHOLOGICAL, AND PARTICLE SIZE ANALYSIS

All of the cement materials were tested in accordance with ASTM C 150. Of the eight Portland cements, six were selected with varying proportions of tricalcium silicate and tricalcium aluminate. One of the cements was also ground to a greater fineness at the cement production facility. To confirm the density of the materials, a Quantachrome Instruments Ultrapyc 1200e pycnometer was used. To determine the crystalline structural of the different Portland cements, all eight were tested in accordance with ASTM C 1365. To determine the gypsum phase, thermo gravimetric analysis and differential thermal analysis (TGA/DTA) were used. A particle size distribution analysis was performed for each of the Portland cements studied in the research.

The results of the chemical composition analysis, the crystalline structure determination and the particle size analysis are presented in Table 1. As can be seen from the data, the difference between the x-ray fluorescence analysis and that from x-ray diffraction is considerable.

4. ISOTHERMAL CONDUCTION CALORIMETRY

To determine the heat produced during the hydration of the eight different Portland cements, isothermal calorimetry was performed in accordance with ASTM C 1702. All of the cements were prepared at a water-to-cement ratio of 0.50 and evaluated at temperatures of 8 °C, 23 °C, and 38 °C.

5. APPARENT ACTIVATION ENERGY OF THE PORTLAND CEMENT PASTE

Apparent activation energy (E_a) was determined by three methods; isothermal conductive calorimetry, per ASTM C 1074, and by the exponential method. The use of isothermal calorimetry testing to determine activation energy has been documented by several researchers. The heat generation from the Portland cement at early ages, determined with the isothermal calorimeter, is used to determine the rate of hydration (k) from linear portions of the heat conduction curves. This method uses a modified Arrhenius equation in which the degree of hydration (α) is assigned a value between 0 and 1, with 0 being equivalent to no hydration having occurred and 1 indicating complete hydration of the cement.
Table 1: Chemical composition, crystalline structure and particle size analysis

<table>
<thead>
<tr>
<th></th>
<th>Cem-1</th>
<th>Cem-2</th>
<th>Cem-3</th>
<th>Cem-4</th>
<th>Cem-5A</th>
<th>Cem-5B</th>
<th>Cem-5C</th>
<th>Cem-6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equivalent Alkalies</td>
<td>0.48</td>
<td>0.41</td>
<td>0.22</td>
<td>0.37</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.35</td>
</tr>
<tr>
<td>C₃S by XRF</td>
<td>50.08</td>
<td>53.67</td>
<td>61.58</td>
<td>57.76</td>
<td>64.45</td>
<td>64.45</td>
<td>64.81</td>
<td>67.96</td>
</tr>
<tr>
<td>C₂S by XRF</td>
<td>20.35</td>
<td>21.69</td>
<td>16.53</td>
<td>17.11</td>
<td>11.23</td>
<td>11.23</td>
<td>11.03</td>
<td>2.52</td>
</tr>
<tr>
<td>C₃A by XRF</td>
<td>8.29</td>
<td>0.00</td>
<td>10.84</td>
<td>3.22</td>
<td>4.81</td>
<td>4.81</td>
<td>4.86</td>
<td>5.74</td>
</tr>
<tr>
<td>C₄AF by XRF</td>
<td>6.98</td>
<td>18.44</td>
<td>0.95</td>
<td>9.81</td>
<td>12.64</td>
<td>12.64</td>
<td>12.65</td>
<td>11.32</td>
</tr>
<tr>
<td>Limestone Addition, %</td>
<td>3.6</td>
<td>0.0</td>
<td>0.0</td>
<td>2.5</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Alite by XRD, %</td>
<td>60.63</td>
<td>56.41</td>
<td>56.24</td>
<td>54.76</td>
<td>58.51</td>
<td>62.44</td>
<td>61.36</td>
<td>57.42</td>
</tr>
<tr>
<td>Belite by XRD, %</td>
<td>12.83</td>
<td>20.38</td>
<td>25.09</td>
<td>24.15</td>
<td>20.23</td>
<td>15.49</td>
<td>16.71</td>
<td>11.35</td>
</tr>
<tr>
<td>Ferrite by XRD, %</td>
<td>7.36</td>
<td>13.71</td>
<td>1.3</td>
<td>9.38</td>
<td>13.91</td>
<td>13.2</td>
<td>12.56</td>
<td>13.24</td>
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<tr>
<td>Free Lime by XRD, %</td>
<td>0.4</td>
<td>0.17</td>
<td>0.13</td>
<td>0.39</td>
<td>0.47</td>
<td>0.69</td>
<td>0.33</td>
<td>0.46</td>
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<tr>
<td>Aluminate (Cubic) by XRD, %</td>
<td>4.95</td>
<td>1.93</td>
<td>6.29</td>
<td>1.66</td>
<td>2.24</td>
<td>3.02</td>
<td>3.24</td>
<td>4.03</td>
</tr>
<tr>
<td>Aluminate (Orthorombic) by XRD, %</td>
<td>2.58</td>
<td>0.5</td>
<td>0.17</td>
<td>0.68</td>
<td>0.53</td>
<td>0.56</td>
<td>0.52</td>
<td>0.43</td>
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<tr>
<td>Calcite by XRD, %</td>
<td>0.81</td>
<td>2.39</td>
<td>1.99</td>
<td>0.58</td>
<td>1.2</td>
<td>1.85</td>
<td>2.14</td>
<td>4.2</td>
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<tr>
<td>Gypsum by XRD, %</td>
<td>2.78</td>
<td>4.05</td>
<td>5.93</td>
<td>3.61</td>
<td>0.00</td>
<td>0.01</td>
<td>0.44</td>
<td>3.29</td>
</tr>
<tr>
<td>Hemihydrate by XRD, %</td>
<td>0.72</td>
<td>0.00</td>
<td>1.09</td>
<td>0.57</td>
<td>0.63</td>
<td>0.61</td>
<td>0.91</td>
<td>1.16</td>
</tr>
<tr>
<td>Anhydrite by XRD, %</td>
<td>0.63</td>
<td>0.00</td>
<td>0.14</td>
<td>0.17</td>
<td>0.81</td>
<td>0.77</td>
<td>0.32</td>
<td>0.12</td>
</tr>
<tr>
<td>Heat Sum</td>
<td>89.47</td>
<td>53.67</td>
<td>113.08</td>
<td>73.08</td>
<td>84.9</td>
<td>87.32</td>
<td>87.89</td>
<td>95.22</td>
</tr>
<tr>
<td>Blaine Fineness, m²/kg</td>
<td>485</td>
<td>238</td>
<td>450</td>
<td>351</td>
<td>524</td>
<td>358</td>
<td>307</td>
<td>389</td>
</tr>
<tr>
<td>Density, C 188 (g/cm³)</td>
<td>3.12</td>
<td>3.18</td>
<td>3.04</td>
<td>3.23</td>
<td>3.16</td>
<td>3.17</td>
<td>3.17</td>
<td>3.09</td>
</tr>
<tr>
<td>Density, Pycnometer (g/cm³)</td>
<td>3.09</td>
<td>3.18</td>
<td>3.04</td>
<td>3.20</td>
<td>3.16</td>
<td>3.17</td>
<td>3.17</td>
<td>3.09</td>
</tr>
<tr>
<td>Median Size (µm)</td>
<td>8.08</td>
<td>13.59</td>
<td>8.71</td>
<td>10.61</td>
<td>8.09</td>
<td>10.72</td>
<td>13.17</td>
<td>10.63</td>
</tr>
<tr>
<td>Mean Size (µm)</td>
<td>9.19</td>
<td>22.45</td>
<td>9.71</td>
<td>12.31</td>
<td>8.82</td>
<td>13.12</td>
<td>19.14</td>
<td>14.45</td>
</tr>
</tbody>
</table>

has been reached. The degree of hydration is calculated as a ratio of the measured heat by the isothermal calorimeter at a time \( t \) to the total heat available as determined by chemical methods as shown in Equation 5.13,14,15 A curve fitting software package (TableCurve 2D) was used to calculate \( \alpha, \beta, \) and \( \tau \).

To determine the apparent activation energy in accordance with the maturity method, ASTM C 1074\(^9\), three sets of mortar cubes were cast and exposed to three different isothermal temperatures. The temperatures chosen for this study were 8 °C, 23 °C, and 38 °C. The TableCurve 2D software package was used to calculate \( S_u, t_0, \) and \( k \) per ASTM C 1074\(^{16}\).

Determining the apparent activation energy by the exponential method is similar to the procedure in ASTM C 1074, though a hyperbolic function is used to fit the strength development data\(^17\). TableCurve 2D was again used to calculate \( S_u, \beta, \) and \( \tau \). This method was solved three different ways. The first method allowed all of the values to vary. The second method allowed all of the values to vary except \( S_u, \) which was held constant. The third method allowed for all of the values to vary except \( S_u \) and \( \tau \), which were both held constant.
A summary of all the apparent activation energy calculations is included in Table 2. The columns shown in the table represent the data collected for the isothermal conductive calorimetry, maturity method using ASTM C 1074\textsuperscript{16}, and the exponential method solved in each of the three ways described above.

<table>
<thead>
<tr>
<th></th>
<th>Isothermal Calorimetry</th>
<th>Maturity</th>
<th>Exp (1)</th>
<th>Exp (2)</th>
<th>Exp (3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cem-1</td>
<td>38,656</td>
<td>44,213</td>
<td>49,218</td>
<td>41,337</td>
<td>38,527</td>
</tr>
<tr>
<td>Cem-2</td>
<td>34,598</td>
<td>31,051</td>
<td>23,204</td>
<td>29,841</td>
<td>40,372</td>
</tr>
<tr>
<td>Cem-3</td>
<td>40,499</td>
<td>36,515</td>
<td>45,336</td>
<td>47,896</td>
<td>35,692</td>
</tr>
<tr>
<td>Cem-4</td>
<td>34,810</td>
<td>19,213</td>
<td>13,364</td>
<td>26,396</td>
<td>23,703</td>
</tr>
<tr>
<td>Cem-5A</td>
<td>30,939</td>
<td>44,213</td>
<td>36,515</td>
<td>55,512</td>
<td>26,238</td>
</tr>
<tr>
<td>Cem-5B</td>
<td>54,568</td>
<td>30,362</td>
<td>35,708</td>
<td>36,199</td>
<td>27,993</td>
</tr>
<tr>
<td>Cem-5C</td>
<td>38,656</td>
<td>44,213</td>
<td>49,218</td>
<td>41,337</td>
<td>38,527</td>
</tr>
<tr>
<td>Cem-6</td>
<td>34,598</td>
<td>31,051</td>
<td>23,204</td>
<td>29,841</td>
<td>40,372</td>
</tr>
</tbody>
</table>

*Note: Exponential (1) allows for all of the values to be variable, Exponential (2) allows for all of the values to vary except $S_u$, and Exponential (3) allows for all of the values to vary except $S_u$ and $\tau$."

### 6. LENGTH CHANGE

Length change measurements were performed on each of the Portland cements studied in the research. To determine the length change for each of the cements, pastes were prepared with water-to-cement ratios of 0.50, and at three different temperatures, to determine the thermodynamic effects of the cement pastes at 8 °C, 23 °C, and 38 °C. The length change testing was divided into three different procedures. The first two procedures consisted of chemical shrinkage and dilatometer shrinkage in order to characterize the performance at early age, using the method developed by Sant, Lura and Wiess\textsuperscript{18}. The last procedure determined the long-term change in length of the cement paste using ASTM C 157\textsuperscript{19} over a 32 week period.

Sant, Lura and Weiss\textsuperscript{18} demonstrated that the standard test methods, like ASTM C 157, do not provide an accurate picture of early-age shrinkage of cement and, if anything, provide a false indication of early-age shrinkage. The test method used in this research utilizes two different approaches for calculating the early-age shrinkage of a cement paste. The first procedure, chemical shrinkage, is designed to examine the cement paste starting shortly after the water is added to the cement and continues until the cement paste has achieved final set. The second procedure, shrinkage in a dilatometer frame, is designed to examine the cement paste from the point of final set until it reaches seven days of age. In order to formulate a
method to correlate the two different procedures, the time of set was determined for each cement. 

Once the two procedures were performed, the length change as determined by the chemical shrinkage method at the time of initial set was established. From that point, the length change was determined from the values obtained using the dilatometer shrinkage procedure until seven days of age.

The standardized test method typically specified for determining the shrinkage potential of Portland cement mortars or concrete is ASTM C 157. This test method requires that the sample be submerged in saturated limewater for a period of 28 days prior to taking any shrinkage readings.

7. DISCUSSION OF RESULTS

Portland cements with similar proportions of tricalcium silicate and tricalcium aluminate, but with varying particle size distributions, were tested and produced similar amounts of power after 3-days of hydration. The finer ground cement produced the least amount of power, while the coarser ground cement produced the most power. Since the crystalline structure and chemistry of the three Portland cements are similar, the only reason for this difference in the amount of power being produced at later ages was the particle size distribution and available surface area for reaction of the different cements. Finer ground cement will produce more power at earlier ages, but will then achieve a higher degree of hydration compared to the other two cements. The coarser ground cement, on the other hand, will produce less power at the earlier ages but then reach a lower degree of hydration compared to the other two cements.

For the cements tested in this research study, the energy of the system increased as the mean particle size decreased or as the Blaine fineness increased. When the data is plotted, a curve materializes such that,

\[ \ln(PSD) = \frac{a_i + b_i}{E_i^2} \]  

(1)

Where:  
PSD = mean particle size  
\( E_i \) = isothermal conductive calorimetry at time, \( t \)  
\( a_i \) = shape factor for time \( t \) (5.299 for 3 days or 5.575 for 7 days)  
\( b_i \) = shape factor for time \( t \) (62.543 for 3 days or 50.140 for 7 days)

When evaluating the activation energy from the Portland cements tested with similar proportions of tricalcium silicate and tricalcium aluminate but with varying particle size distributions, it appears that the best method for predicting the activation energy is the x-ray diffraction data. All of the other methods predicted that the medium ground cement (Cem-5B) had lower activation energy than the finer ground cement.

For calculating the isothermal calorimetry method, the available heat produced by cement could be updated to include a Blaine Fineness value. For the three different cements tested, an equation was formulated that would better estimate the available heat produced:
Hcem = 500·pC3S +260·pC2S + 866·pC3A + 420·pC4AF + 624·pSO3 + 1186·pFreeLime + 850·pMgO + 1487·pBlaineFineness

From the measured results, the total length change through 32-weeks can be calculated by adding the early-age shrinkage with the long-term shrinkage. This provides a method for determining the total shrinkage produced by a Portland cement. Total shrinkage results were calculated for each of the Portland cements and are presented in Table 3.

Table 3: Total length change measurements

<table>
<thead>
<tr>
<th></th>
<th>Early-age Shrinkage (µε)</th>
<th>Long-term Shrinkage (µε)</th>
<th>Total Shrinkage (µε)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 °C</td>
<td>23 °C</td>
<td>38 °C</td>
</tr>
<tr>
<td>Cem-1</td>
<td>12000</td>
<td>9240</td>
<td>3850</td>
</tr>
<tr>
<td>Cem-2</td>
<td>6580</td>
<td>4320</td>
<td>2550</td>
</tr>
<tr>
<td>Cem-3</td>
<td>7450</td>
<td>4760</td>
<td>3280</td>
</tr>
<tr>
<td>Cem-4</td>
<td>4630</td>
<td>3020</td>
<td>2080</td>
</tr>
<tr>
<td>Cem-5A</td>
<td>5680</td>
<td>3800</td>
<td>2880</td>
</tr>
<tr>
<td>Cem-5B</td>
<td>6590</td>
<td>4350</td>
<td>2900</td>
</tr>
<tr>
<td>Cem-5C</td>
<td>6790</td>
<td>4510</td>
<td>3010</td>
</tr>
<tr>
<td>Cem-6</td>
<td>9980</td>
<td>7040</td>
<td>4070</td>
</tr>
</tbody>
</table>

It was determined that approximately 90% of the total shrinkage occurs in the first seven days. ASTM C 15719 does not capture this information. By evaluating the data, it can be determined that Portland cements that are placed and cured in colder environments will exhibit a higher degree of shrinkage. In some cases, dropping the temperature by 15 °C almost doubled the total amount of shrinkage that occurred in a Portland cement.

It can be seen from the three cements with similar tricalcium silicate and tricalcium aluminate proportions, but with varying particle size distributions, that the grind of the cement does have an effect on total length change. As the mean particle size increased, the total length change decreased by approximately 10% for the cements tested. The cements with the higher amounts of tricalcium aluminate exhibited higher degrees of shrinkage. The cement with the highest amount of shrinkage was the cement with the highest tricalcium aluminate and highest tricalcium silicate proportions.

8. CONCLUSIONS

The current standard specifications for determining the amount of heat that will be produced by a given cement needs to be re-evaluated to take Blaine fineness or mean particle size distribution into consideration. The mean particle size of a Portland cement does have an effect on total shrinkage, but is not as significant as the chemical composition of the cement. This information can provide valuable input parameters for modeling and predicting the amount of heat produced, activation energy, and total length change of a Portland cement with respect to performance based specifications.
The current procedure for estimating 335 kJ/kg [80 cal/g] does not demonstrate the actual amount of heat that can be produced, nor will it give a good estimate of the activation energy. The most appropriate method for determining activation energy is the hyperbolic method utilizing the data collected from x-ray diffraction analysis. The most effective way to determine the amount of shrinkage that will occur due to the composition of the cement is through testing the materials for chemical shrinkage combined with shrinkage measured in the dilatometer frame.

REFERENCES


