How to capture the HoH for the first hour

Lars Wadso and Paul Sandberg
Why do we want to measure the heat production during the first hour (minutes) of hydration?

1. We are interested in what happens during the early stages of hydration (sulfate aluminate control, admixtures, ...)

2. When measuring the heat of hydration during, e.g., 7 days, we also need to accurately measure and include the early heat production.
Internal mixing vs. external mixing
Internal mixing

[Images of internal mixing equipment and a person demonstrating the process]

Internal mixing video
Out of range
Very early dissolution and reaction processes
Negative initial thermal powers (evaporation)
Thermal power and heat of mixing

Mixing 30 s ≈ 0.01 h
Initial thermal power can be very much higher than the main peak (but of much, much duration)
The kinetics of rapid events are distorted by the thermal inertia of the sample+calorimeter (Tian correction improves the dynamics to a certain extent)

Mixing 30 s \approx 0.01 \text{ h}
1. Possible to study the hydration processes from time zero.

1. Baseline can shift compared to closed vial measurements; and it is maybe not appropriate to use the "dry" baseline before injection.
2. Very low intensity mixing.
3. Stiff mixes cannot be made.
4. Significantly more time consuming compared to closed vial measurements.
Early Age Reaction: Aging of the Sample?

- 1 month
- 3 months
- 6 months

Cement Hydration

STK 1, #591
Tue Nov 9 14:58:44 CET 2004

If not explicitly mentioned, the cement was measured with w/c=0.4, 20 C

* mixed with Stirrer Unit
Several factors may contribute to the measurement error obtained from external mixing

Heat exchange with lab surrounding while mixing
The longer the materials are kept outside the calorimeter, the larger the impact. Large relative impact (heat exchange per gram cement) on a small sample vs a large sample

Mixing energy
External mixing may transfer relatively more mixing energy to the sample, since internal mixing is generally thought to be less intensive.

Heat exchange with external mixing equipment
The temperature of the mixing equipment is controlled by the ambient lab temperature, which is typically only specified within 21-25°C (US) or 18-22°C (EU). As a consequence, an externally mixed sample may exchange significant heat with the mixing equipment during mixing.

Sample composition error from transfer of cement paste to calorimeter vial
Segregation while transferring a sub sample from the mixing container to the calorimeter. This is especially apparent for very fluid cement paste when using a pipette to transfer the sample.

Water and cement temperature differs from that of the calorimeter
A comparably large error may occur when water and cement is not pre-conditioned to the same temperature as the calorimeter before mixing. ASTM C1702 requires water within 0.2°C and cement within 1.0°C of the calorimeter while the draft European isothermal calorimetry method allows up to 0.7°C temperature difference between the calorimeter and the materials.
### Common external cement paste mixing methods

**Standard EN 196 mixing with a Hobart mixer (6000 g).**

- Mixing 60 s with a hand-held household mixer

**High shear mixing ASTM C1738**

**In-vial Vortex mixing of materials weighed directly into test vial**

**In-vial hand mixing of materials weighed directly into test vial**

### Pro’s and con’s for these external paste mixing methods

<table>
<thead>
<tr>
<th>+ well known standard, equivalent</th>
<th>Fast, inexpensive</th>
<th>Very repeatable, especially with admixtures</th>
<th>Fast, very small heat loss</th>
<th>Fast, very small heat loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poor mixing, segregation, heat exchange</td>
<td>Segregation, heat exchange</td>
<td>Must cool to prevent large temp rise</td>
<td>Inadequate mixing with admixture</td>
<td>Inadequate mixing with admixture</td>
</tr>
</tbody>
</table>
Issue with thermal mis-match at room temperature

Heat exchange with lab surrounding while mixing
Issue with thermal mis-match at elevated temperature

Heat exchange with lab surrounding while mixing

RILEM procedure for pozzolanic activity uses external mixing at room temperature, testing at 40°C.

- Temperature mis-match between externally mixed sample and isothermal calorimeter is reduced when using in-vial external mixing with pre-conditioned material, and eliminated for all practical purposes when using Calmetrix semi-automated internal mortar mixer.
**ASTM C1702 effect of external mixing methods for cement paste**

<table>
<thead>
<tr>
<th></th>
<th>Hobart</th>
<th>Hand held blender</th>
<th>High shear blender</th>
<th>In-vial vortex mix</th>
<th>In-Vial hand mix</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calorimetry sample</td>
<td>5-10 g</td>
<td>5-10 g</td>
<td>5-10 g</td>
<td>5-10 g</td>
<td><strong>50 g</strong></td>
</tr>
<tr>
<td>External mix time</td>
<td>minutes</td>
<td>30-60 s</td>
<td>30-60 s</td>
<td>30 s</td>
<td>30 s</td>
</tr>
<tr>
<td>Mixing energy</td>
<td>small</td>
<td>medium</td>
<td>large</td>
<td>small</td>
<td>small</td>
</tr>
<tr>
<td>Heat exchange</td>
<td>large</td>
<td>medium</td>
<td>medium</td>
<td>small</td>
<td>small</td>
</tr>
<tr>
<td>Sampling error</td>
<td>large if segregation</td>
<td>large if segregation</td>
<td>large if segregation</td>
<td>none</td>
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**Repeatability between labs**

**without** preconditioning water and cement before mixing

<table>
<thead>
<tr>
<th></th>
<th>1 h CoV, %</th>
<th>24 h CoV, %</th>
<th>3 d CoV, %</th>
<th>7 d CoV, %</th>
</tr>
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<tbody>
<tr>
<td>1 h CoV</td>
<td>18%</td>
<td>9%</td>
<td>7%</td>
<td>6%</td>
</tr>
<tr>
<td>24 h CoV</td>
<td>15%</td>
<td>8%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>7 d CoV</td>
<td>[25%]</td>
<td>[2%]</td>
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**with** preconditioning water and cement before mixing

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<tr>
<td>1 h CoV</td>
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<td>7%</td>
<td>6%</td>
<td>6%</td>
</tr>
<tr>
<td>24 h CoV</td>
<td>10%</td>
<td>6%</td>
<td>4%</td>
<td>4%</td>
</tr>
<tr>
<td>3 d CoV</td>
<td>no data</td>
<td>no data</td>
<td>3%</td>
<td>2%</td>
</tr>
<tr>
<td>7 d CoV</td>
<td>no data</td>
<td>no data</td>
<td>4%</td>
<td>2%</td>
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**Recommendations:**

- **Pre-condition inside calorimeter before mixing**
- **Mix directly in sample vial**

**Table:**

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**Notes:**

- CoV: Coefficient of Variation
- Pre-conditioning water and cement before mixing
- No data indicated in the table.
How do current standards deal with potential errors from external mixing?

**ASTM C1702 Heat of hydration using isothermal calorimetry**

The mix water and cementitious material shall be conditioned to the same temperature as the calorimeter within 0.2° C and 1.0° C, respectively, before mixing. ASTM recommends storing water inside the calorimeter for several hours before mixing.

ASTM eliminated correction factors after a very extensive Round Robin (15 labs, 368 tests) in 2012 concluded that the correction has no merit, **provided that the mix water temperature is tightly controlled**. Specifically, the correction was on average 2 J/g with 6 J/g standard deviation, while the corresponding standard deviation without the correction was also 2 J/g when the mix water temperature was tightly controlled, compared to 9 J/g when only considering samples prepared with mixing outside the vial, without tight temperature control of mix water. The average difference between internal and external mixing was 2 J/g at 1 h, but the standard deviation was actually higher for internal mixing.

**CCRL Reference cement**

The CCRL reference cement reports HoH at 1 h to allow users to compare HoH at 1, 3, and 7 days excluding the less reproducible heat during the first hour. The standard deviation at 1 h for in-vial external mixing was 1.5 J/g compared to 3.5 J/g for internal mixing, using pre-conditioned water.

**ASTM C563 Sulfate optimization – isothermal calorimetry**

ASTM C563 allows for using Heat of Hydration by isothermal calorimetry, among other methods. When using isothermal calorimetry with cement paste, in-vial mixing is recommended. The user is asked to remove the heat before the end of the dormant period as it improves the precision of the method.
How much of a problem is the “First peak error”?

Get an idea by considering the following tests in your calorimeter:

- Condition the mix water at the lowest temperature allowed
- Condition the mix water at the highest temperature allowed
- Do the same for the cement
- Do the same for both the mix water and the cement
- Compare against mix water conditioned inside the calorimeter
- Compare against cement conditioned inside the calorimeter
- Compare against mix water and cement conditioned inside the calorimeter
- Evaluate at 1h, 24h, 48h, 72h, 7 days