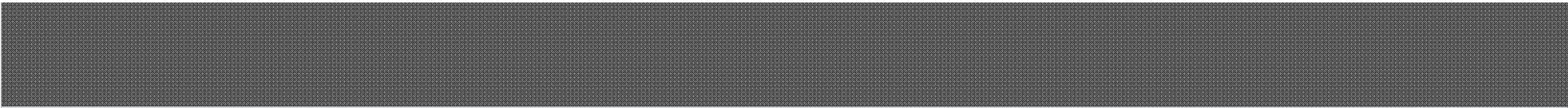




How to capture the HoH for the first hour

Lars Wadso and Paul Sandberg

calmetrix

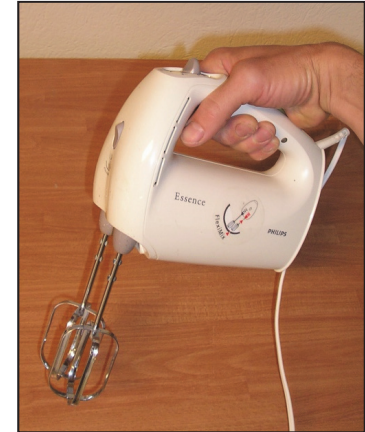
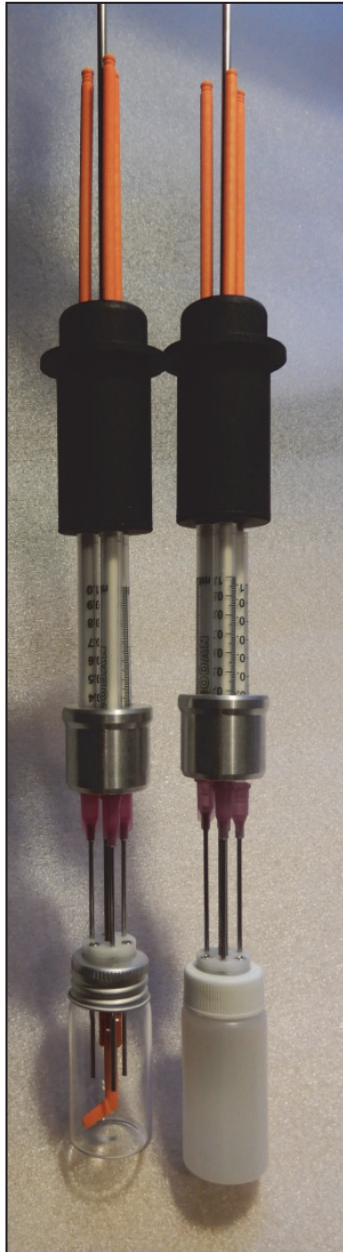


Why do we want to measure the heat production during the first hour (minutes) of hydration?

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

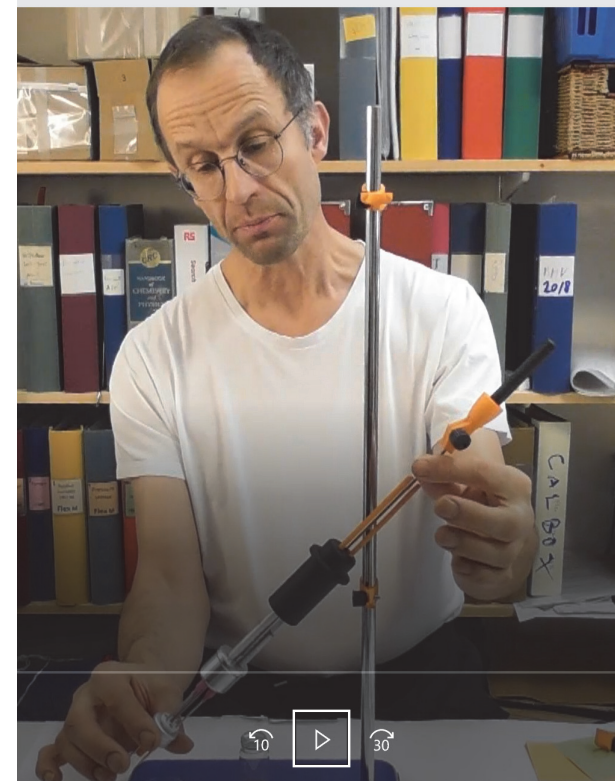


calmetriX

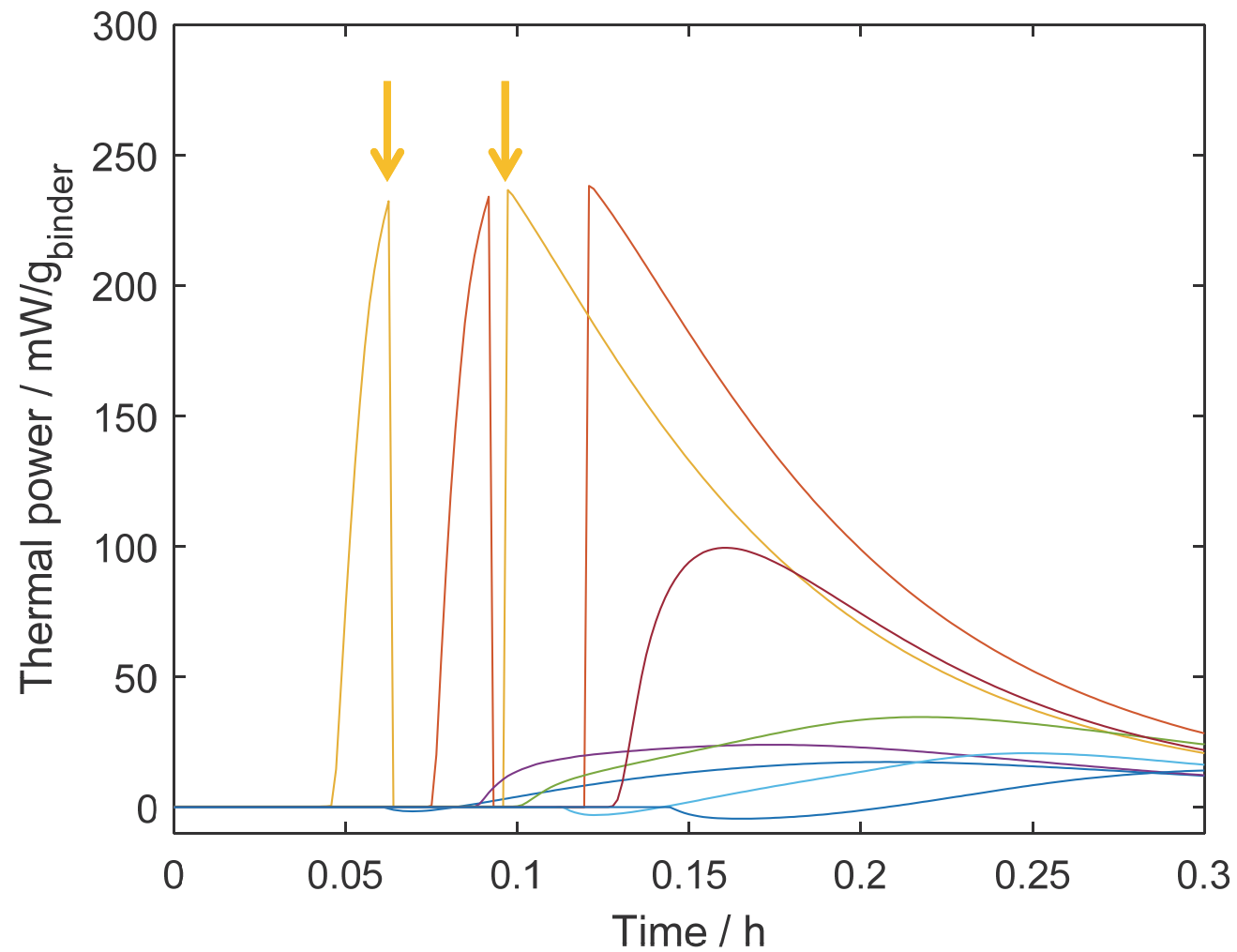
Internal mixing



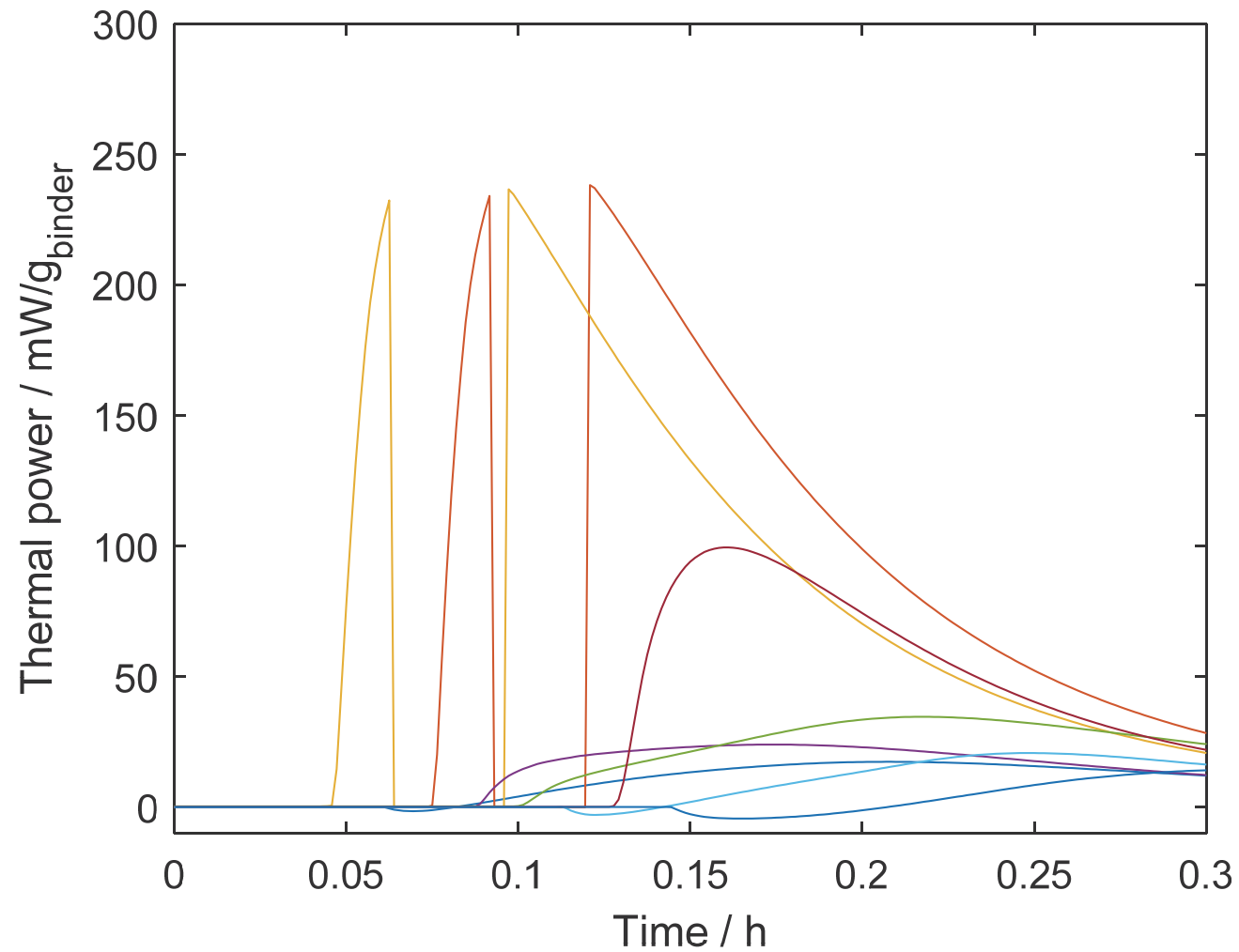
[Internal mixing video](#)



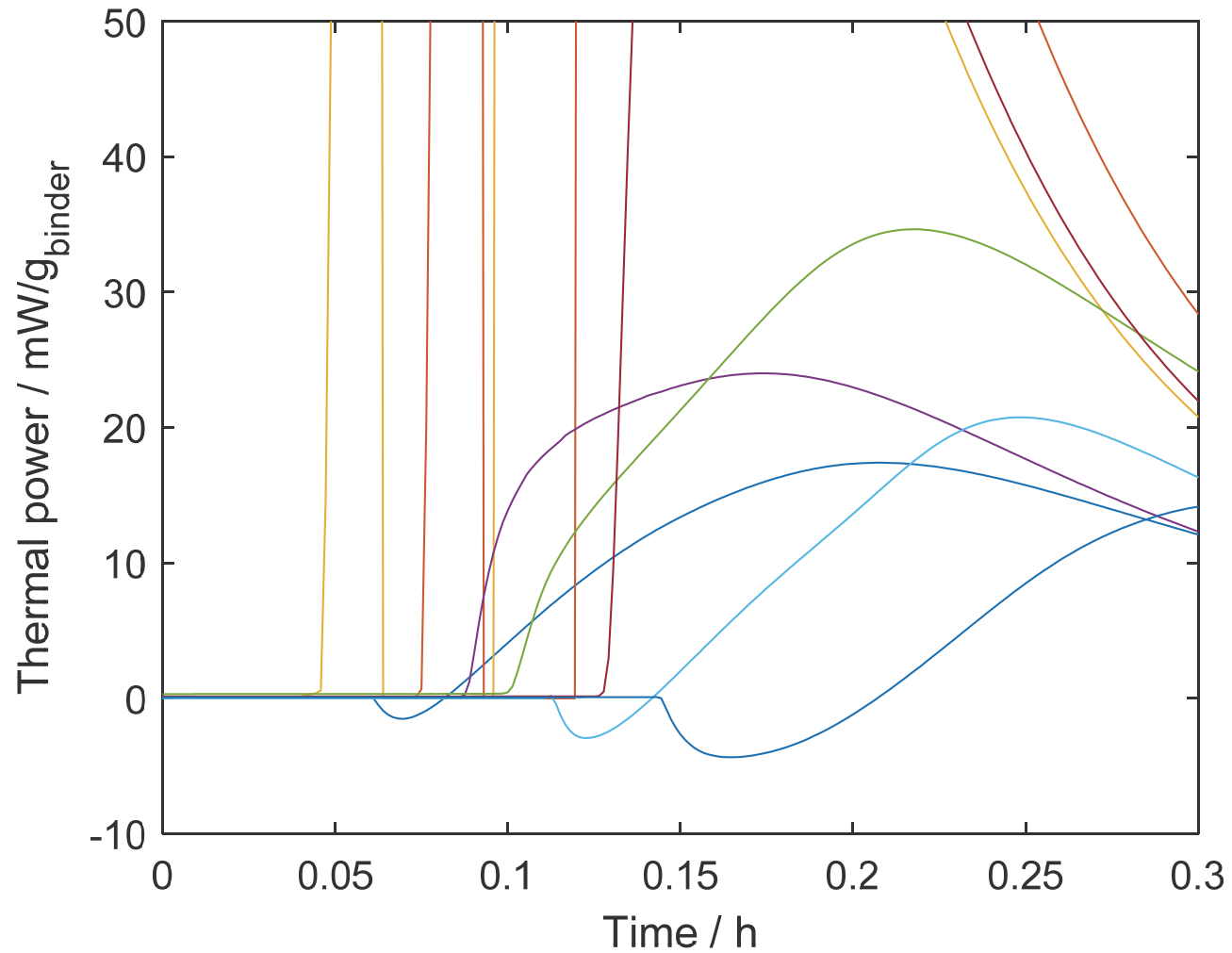
Out of range



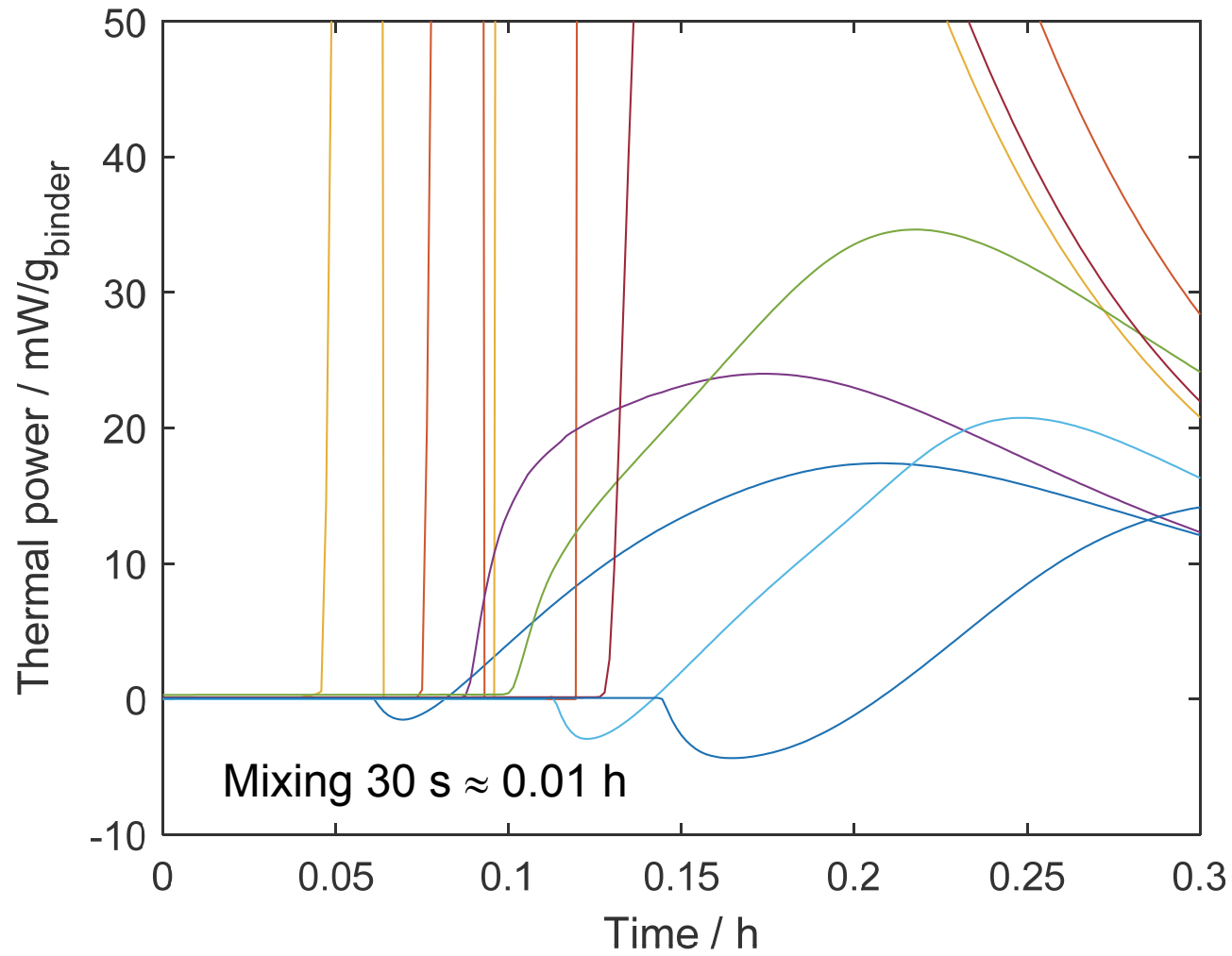
Very early dissolution and reaction processes



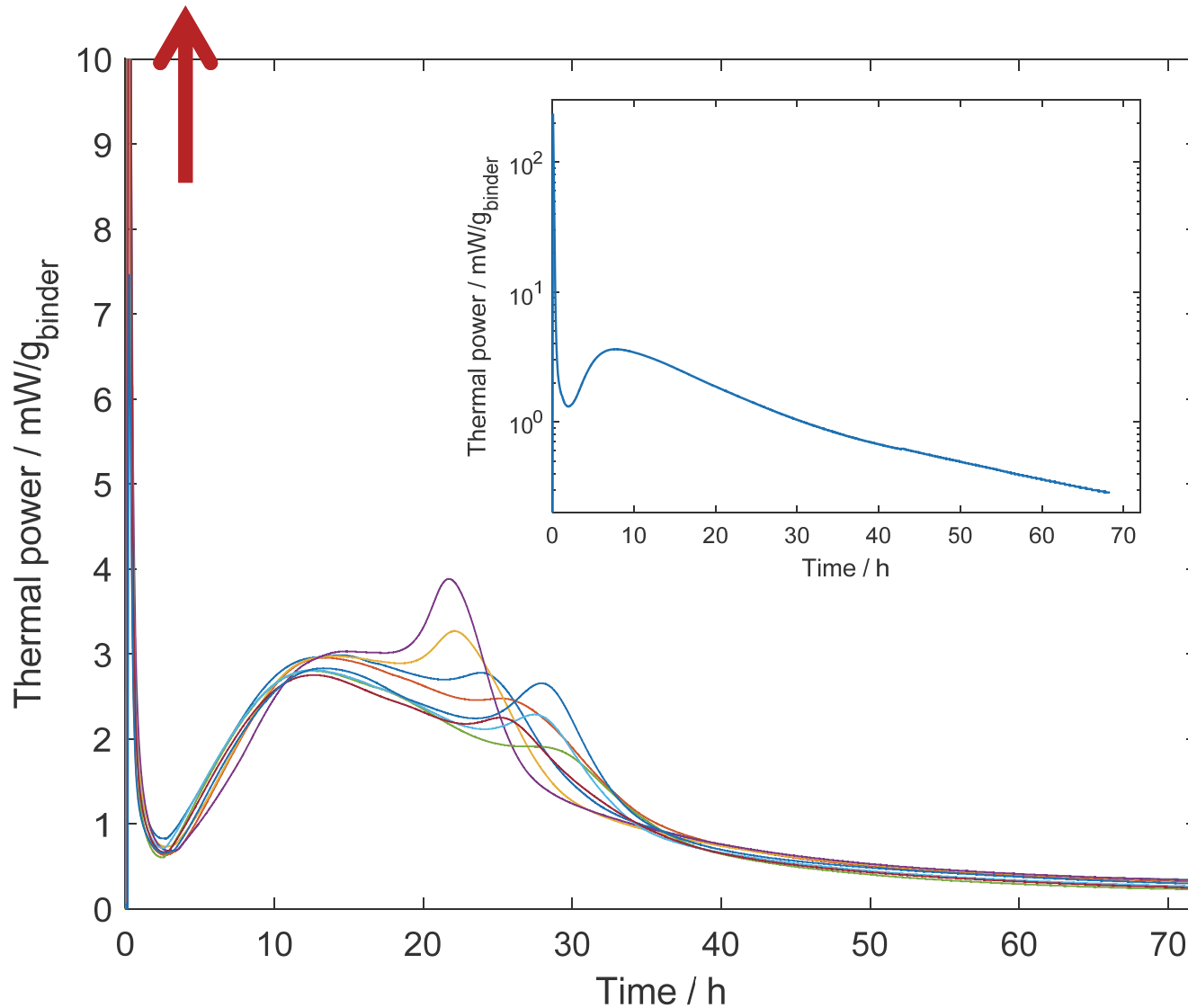
Negative initial thermal powers (evaporation)



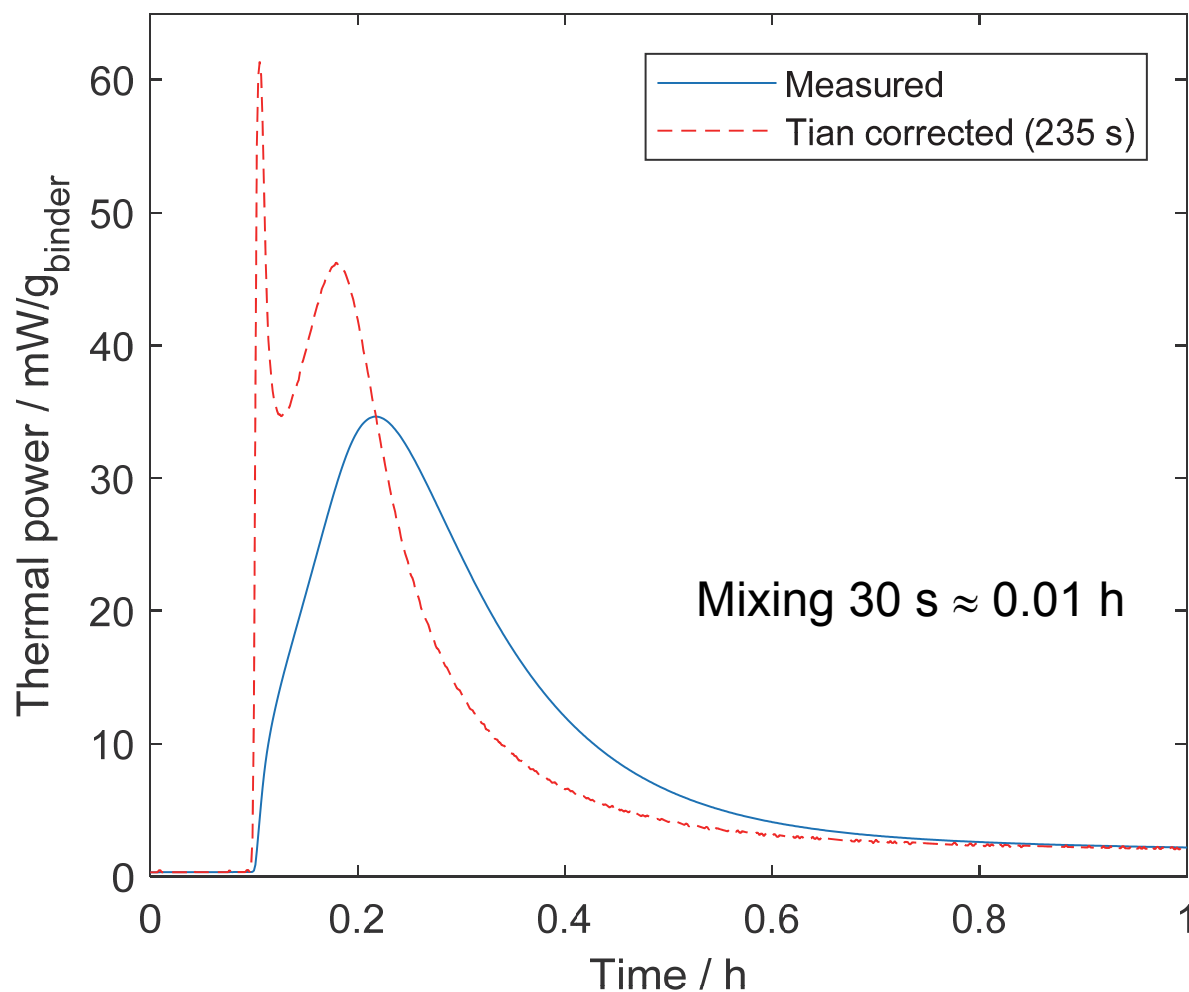
Thermal power and heat of mixing



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)



Pro's and con's for internal vs external mixing

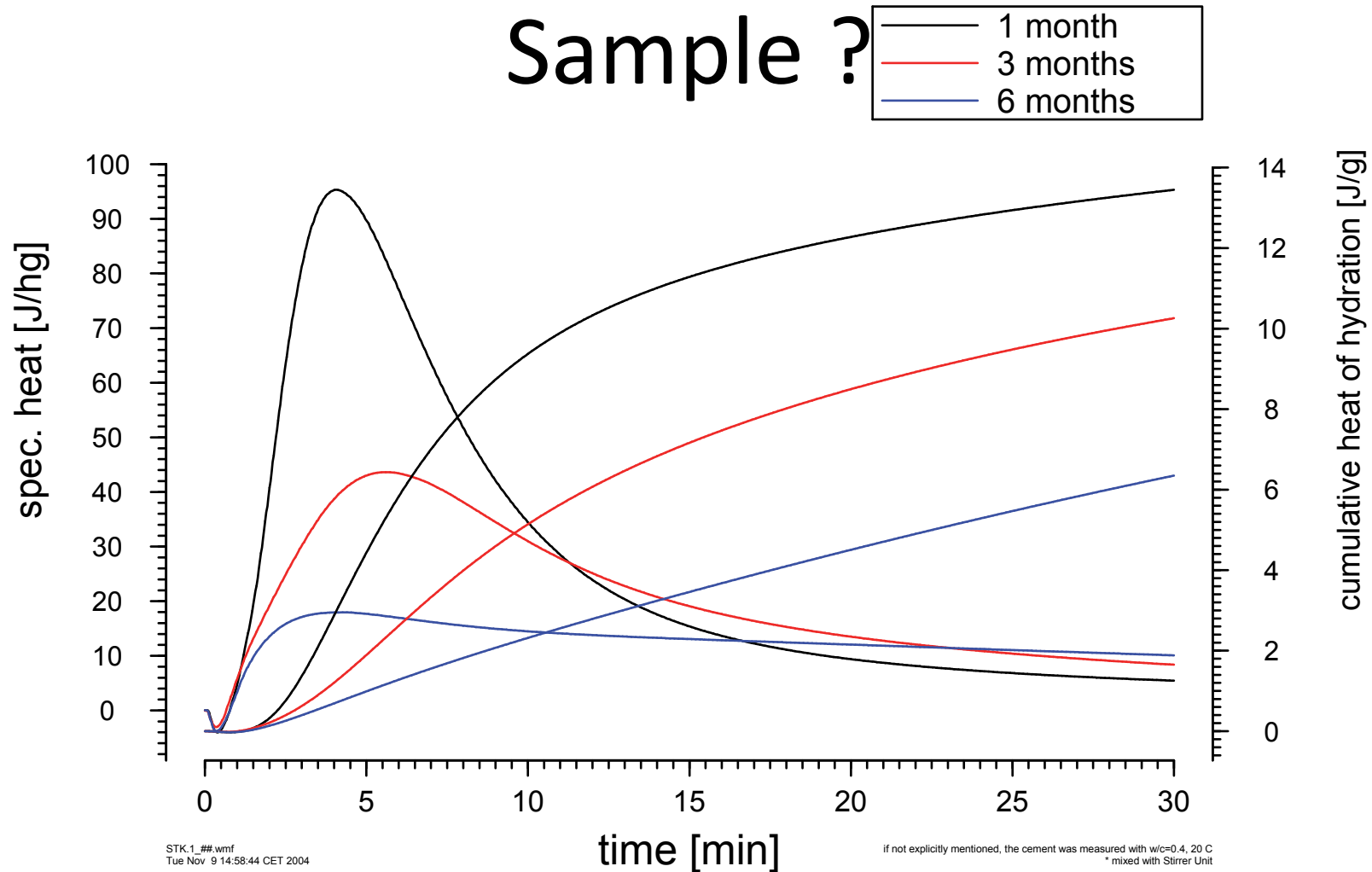


1. Possible to study the hydration processes from time zero.



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 ?



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 21-25C (US) or 18-22C (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.

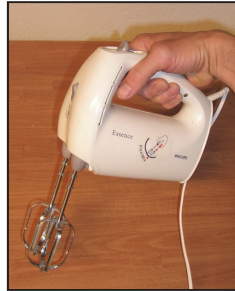
Water and cement temperature differs from that of the calorimeter

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 0.2C 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).



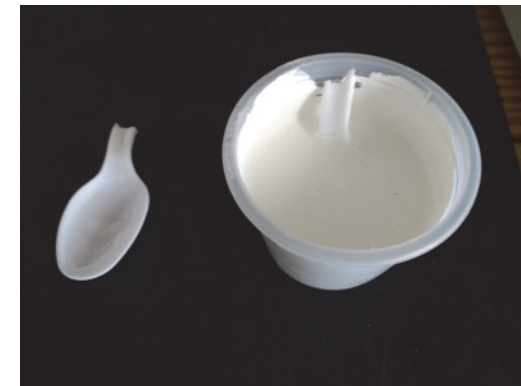
Mixing 60 s
with a hand-
held
household
mixer



High shear
mixing
ASTM
C1738



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



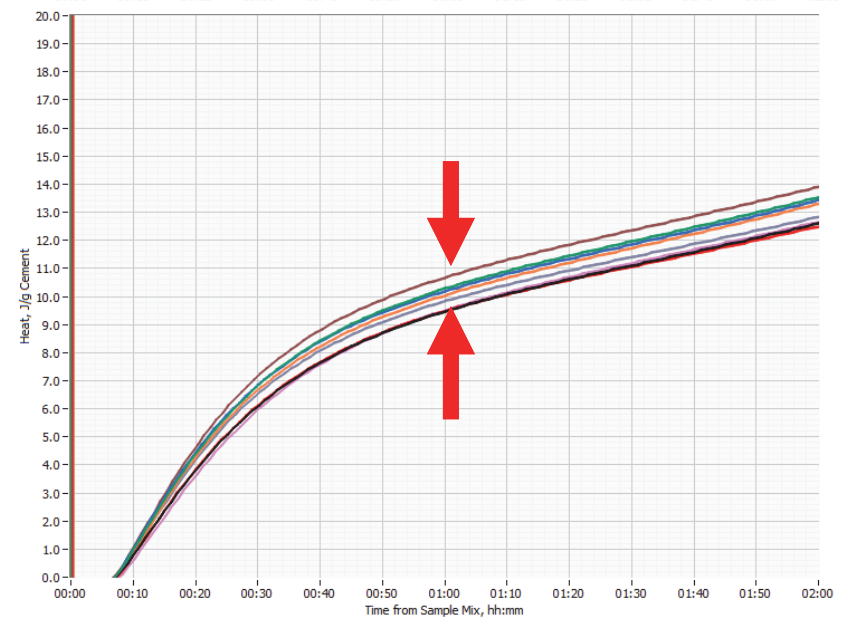
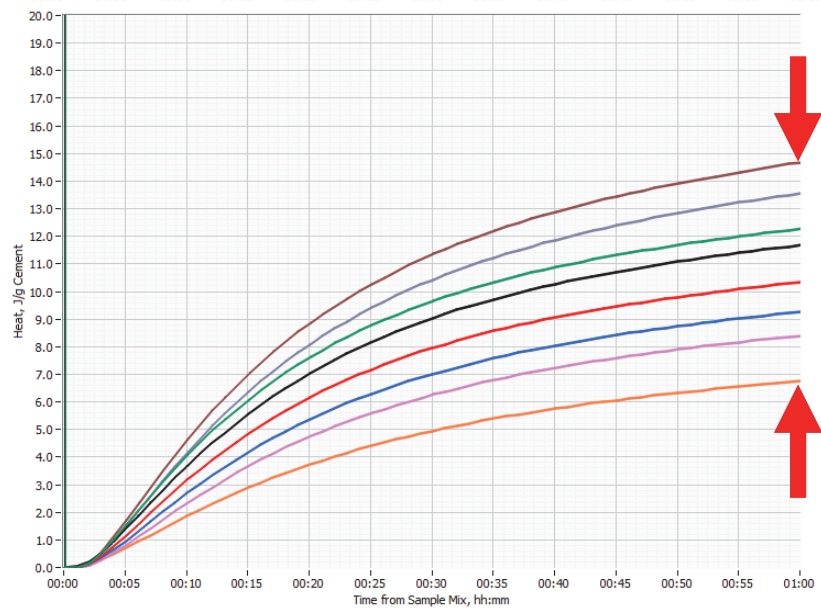
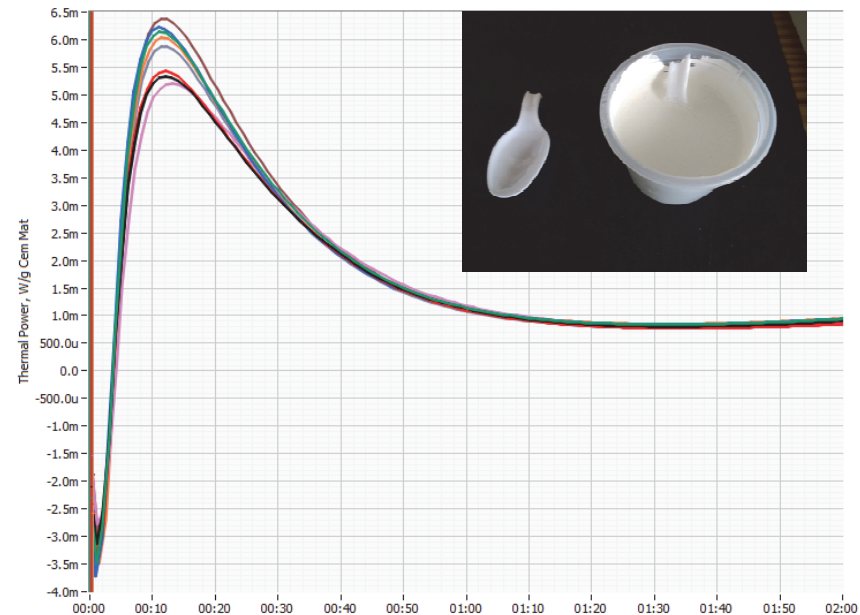
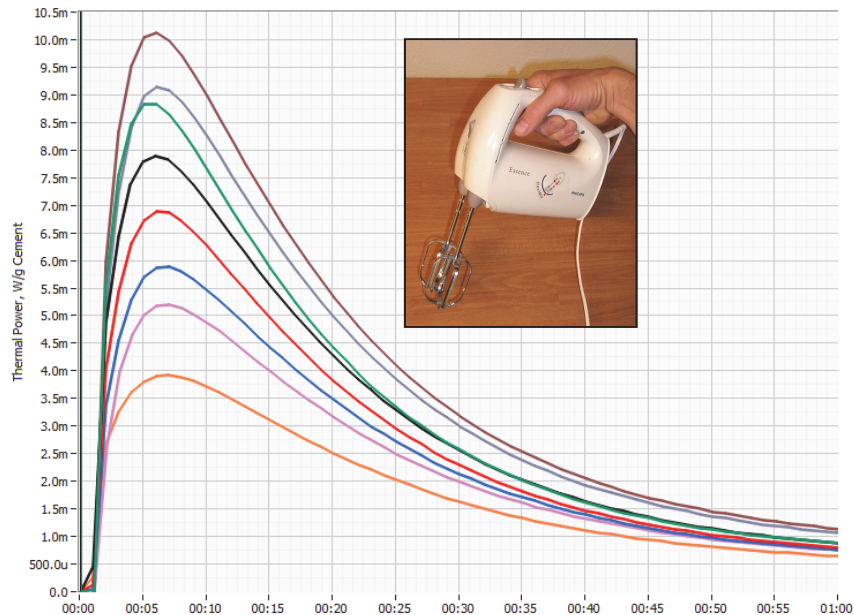
In-vial hand mixing of
materials weighed
directly into test vial
with spoon left inside
test vial

Pro's and con's for these external paste mixing methods

<div style="color: green; font-size: 2em; margin-bottom: 5px;">+</div> <div style="color: red; font-size: 2em; margin-bottom: 5px;">-</div>	well known standard, equiplent	Fast, inexpensive	Very repeatable, especially w admixtures	Fast, very small heat loss	Fast, very small heat loss
	Poor mixing, segregation, heat exchange	Segregation, heat eachange	Must cool to prevent large temp rise	Inadequate mixing with admixture	Inadequate mixing with admixture

Issue with thermal mis-match at room temperature

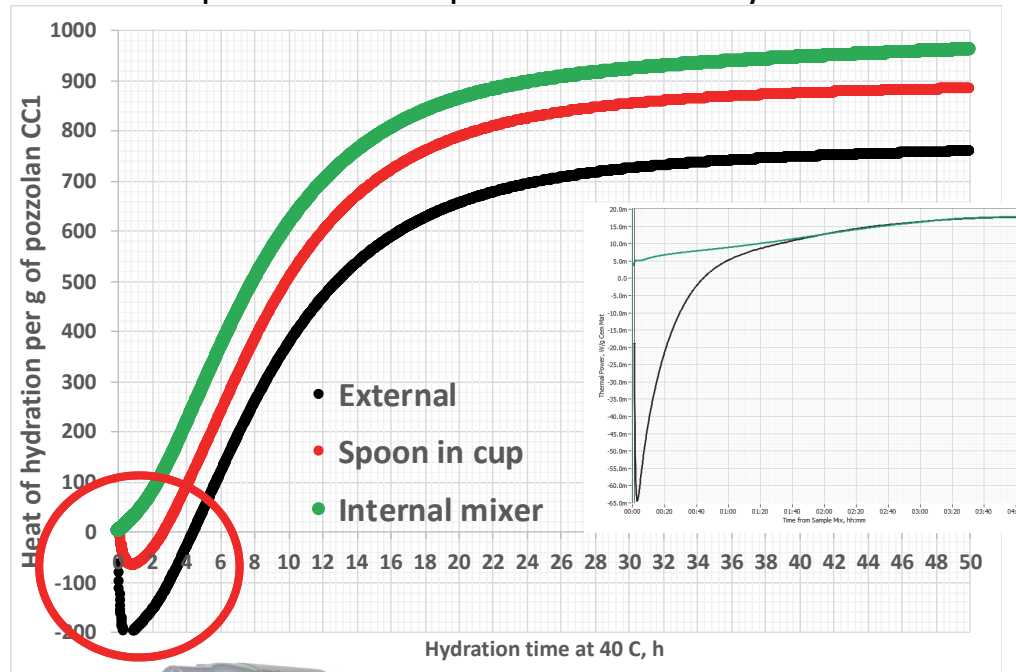
Heat exchange with lab surrounding while mixing



Issue with thermal mis-match at elevated temperature

Heat exchange with lab surrounding while mixing

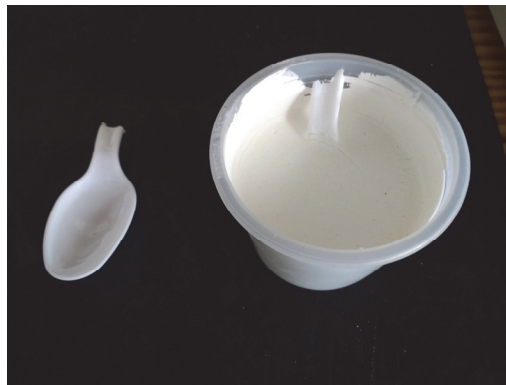
RILEM procedure for pozzolanic activity uses external mixing at room temperature, testing at 40 C



- 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



Traditional external mixing

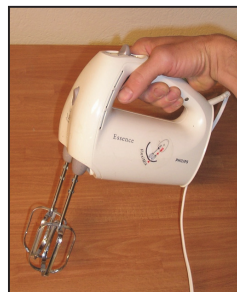


In-vial external mixing



Calmetrix semi-automated internal mortar mixer CalmetriX

ASTM C1702 effect of external mixing methods for cement paste



	Hobart	Hand held blender	High shear blender	In-vial vortex mix	In-Vial hand mix
Calorimetry sample	5-10 g	5-10 g	5-10 g	5-10 g	50 g
External mix time	minutes	30-60 s	30-60 s	30 s	30 s
Mixing energy	small	medium	large	small	small
Heat exchange	large	medium	medium	small	small
Sampling error	large if segregation	large if segregation	large if segregation	none	none

Repeatability between labs **without** preconditioning water and cement before mixing

1 h CoV, %	18%	15%	[25%]	10%	no data
24 h CoV, %	9%	8%	[2%]	6%	no data
3 d CoV, %	7%	6%	[2%]	4%	no data
7 d CoV, %	6%	6%	[2%]	5%	no data

Repeatability between labs **with** preconditioning water and cement before mixing

1 h CoV, %	10%	10%	no data	6%	5%
24 h CoV, %	7%	6%	no data	2%	2%
3 d CoV, %	6%	4%	no data	3%	2%
7 d CoV, %	5%	5%	no data	4%	2%

Recommendations:

Pre-condition inside calorimeter before mixing

Mix directly in sample vial

calmetrix

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