The use of isothermal calorimetry in cement production

Paul Sandberg

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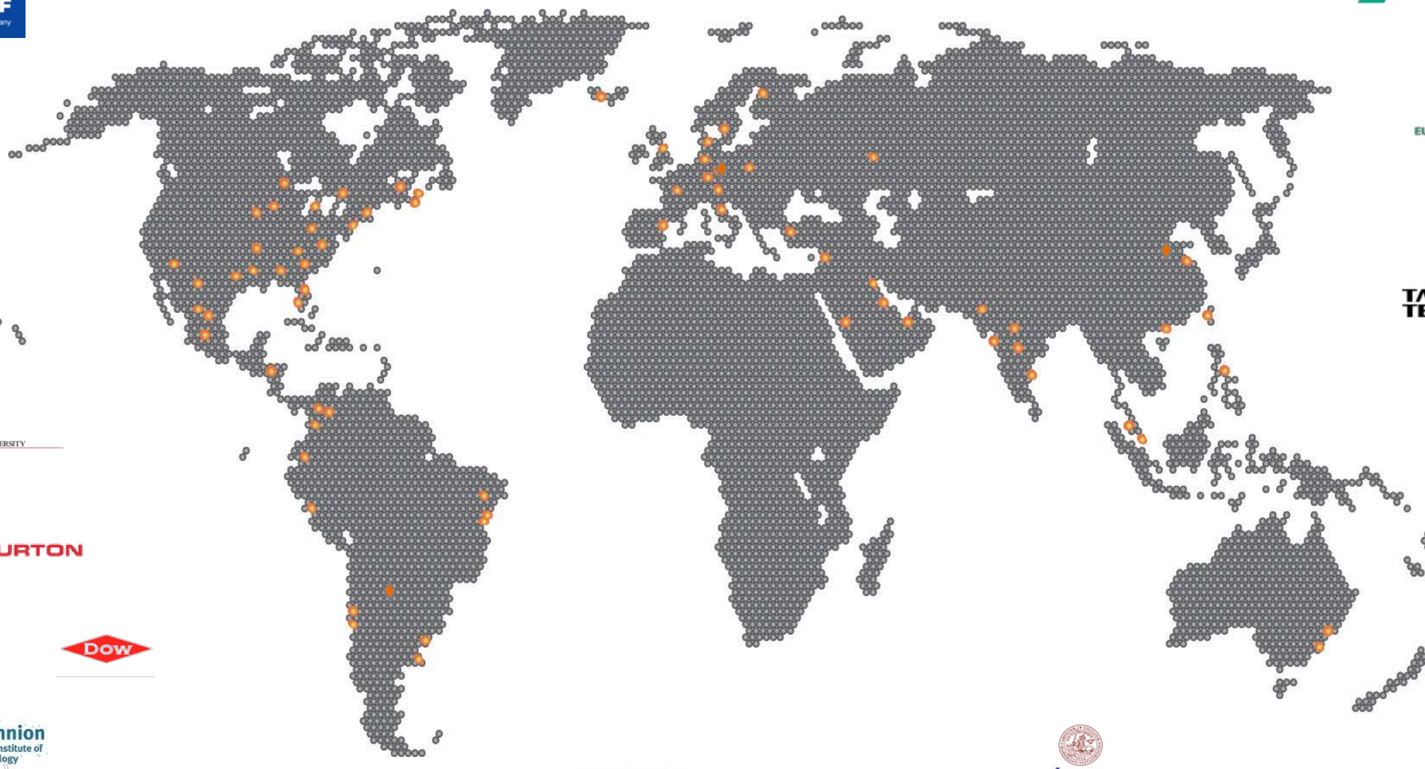
Calmetrix products are used where cement is: around the world …

CALMETRIX PRODUCTS IN USE AROUND THE WORLD



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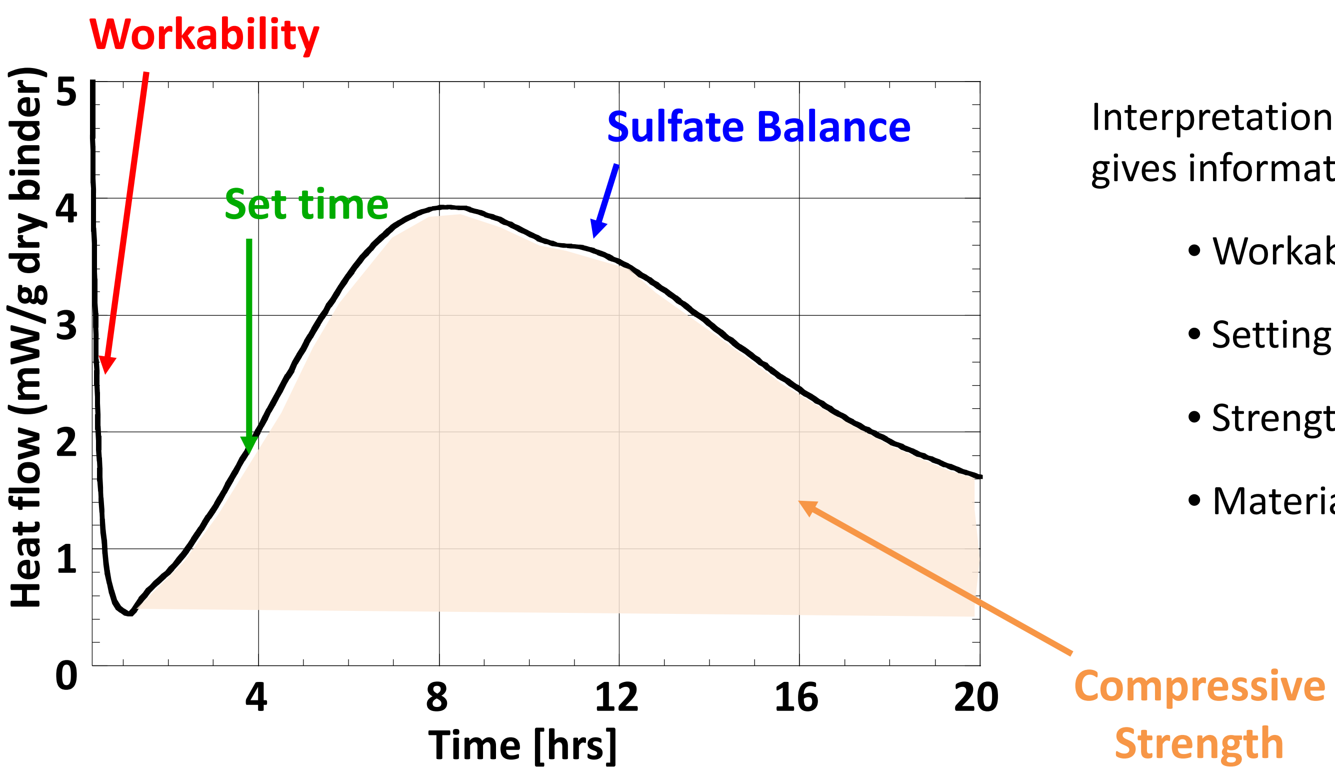
What is calorimetry?

What is calorimetry?

Almost all chemical reactions & physical transformation involve heat release or uptake – often proportional to the amount of reaction. The measurement and interpretation of this heat exchange is the science of “calorimetry”

A Calorimetry curve indicates a number of concrete quality parameters



Interpretation of a calorimetry curve gives information about:

- Workability
- Setting time
- Strength gain
- Material incompatibility

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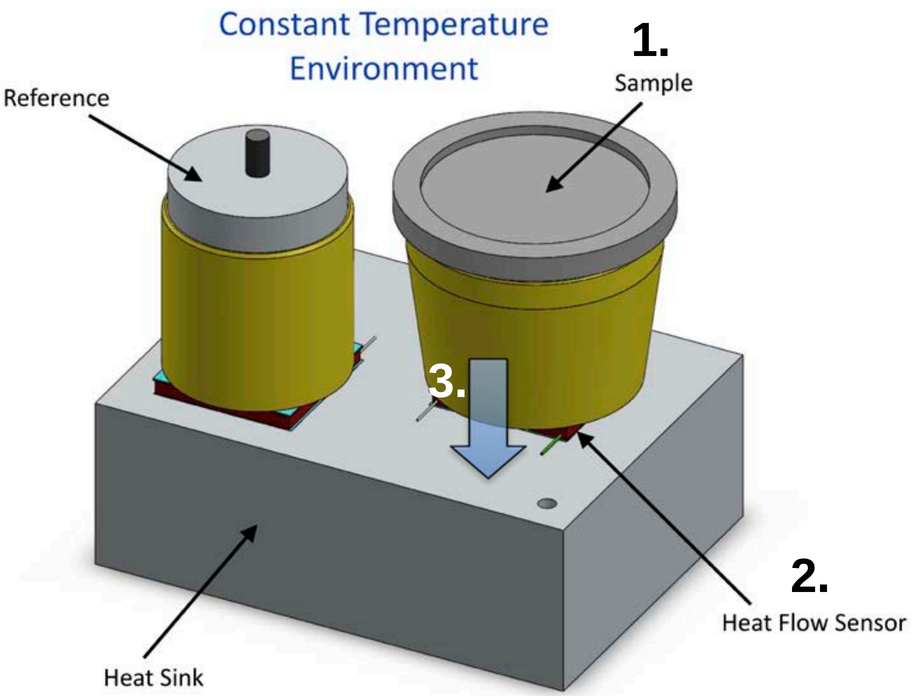
Principles of an isothermal calorimeter

Schematics of an isothermal calorimeter



1. Heat is produced in the sample...
2. and a small temperature difference develops across the heat flow sensor…which results in a voltage output...
3. while heat flows to the heat sink.

- **The isothermal calorimeter operates at near-constant temperature**
- **Most instruments allow a wide range of operating temperatures**
- **You need to select test temperature well in advance of your test!**

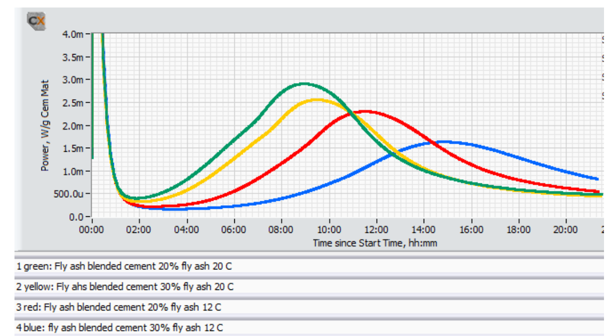
Uses of calorimetry: R&D and Quality Control

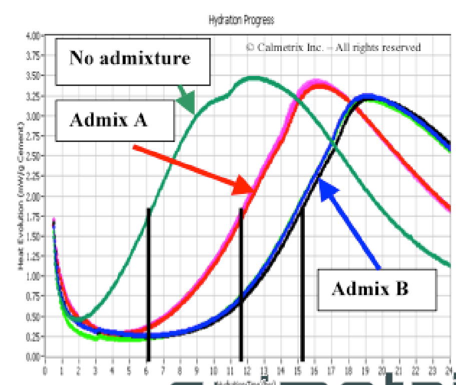
Calorimetry is like taking the Blood Pressure of Cement

- Simple Low cost method for measuring the rate of cement hydration, ***with no laboratory required.***
- Level of Hydration will determine rate of set and strength development.
- Used to measure effects of materials and mix design on reactivity

Some basic uses of isothermal calorimetry

- ***Heat of Hydration ASTM C1702***
- ***Sulfate optimization***
- Temperature effects – winter vs summer formulations
- Early stiffening – co additives, raw materials selection, formulation
  - *Special procedure to capture very early hydration effects*
- ***Accelerator formulations – concrete, cement, shotcrete***
- Cement – SCM – admixture incompatibility
- Customer Service – troubleshooting ASTM C 1679





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How to read calorimetry power and energy graphs

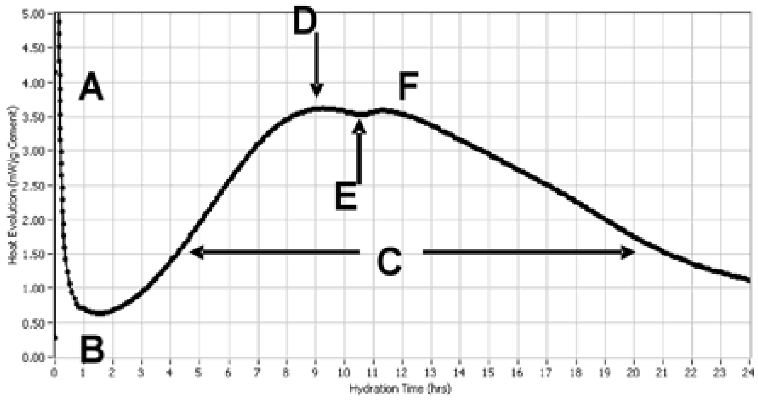

Fig-1: Isothermal calorimetry thermal power graph of a typical cement in sulfate balance

Thermal power graph

- Shows the *RATE* of cement hydration, as affected by temperature, sulfate, other active materials such as admixture, SCM, etc
- Very easy to detect by calorimetry, typically not seen by compressive strength testing

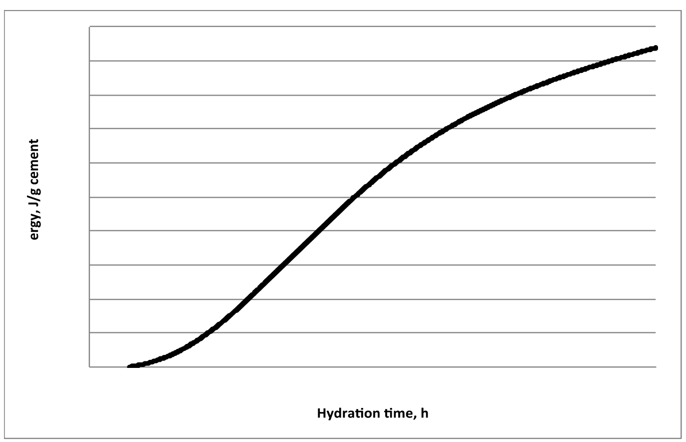

Fig-2: Isothermal calorimetry heat (energy) graph of a typical cement in sulfate balance

Heat (energy) graph

- Shows the degree of reaction, e.g. degree of cement hydration, which correlates with mechanical property development
- Hydration before set is not considered to contribute to mechanical properties, hence excluded ***except when investigating early stiffening issues***

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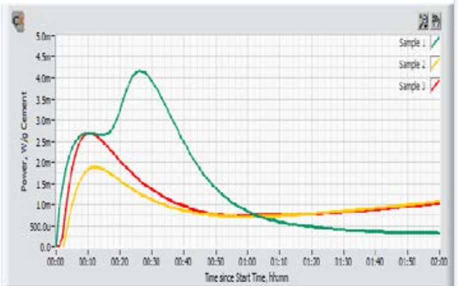
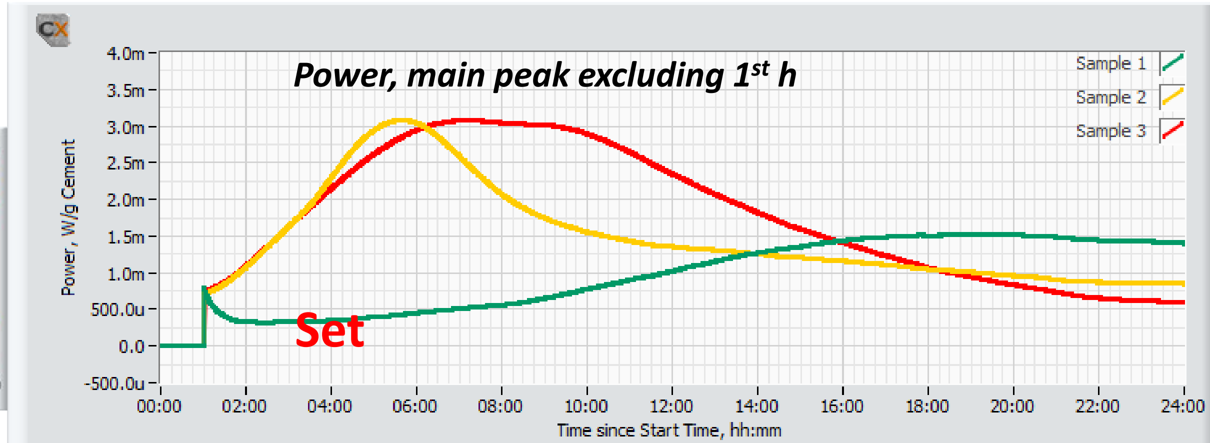
Isothermal calorimetry – Basic interpretation

By integrating the thermal power curve – measuring the area under the power curve – we get "Energy", or "Heat of Hydration" in cement terms.



1st peak 0-2 h

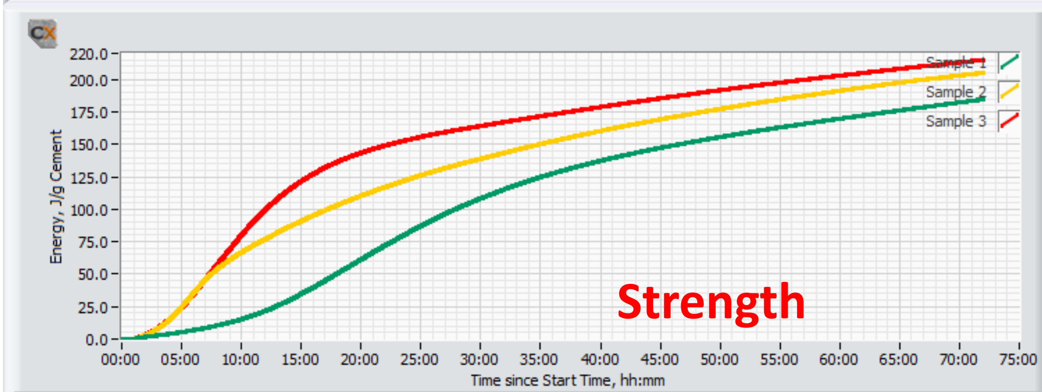
Workability loss



1 green: Cement as-is, no additional sulfate

2 yellow: Cement with 1% SO3 added as calcium sulfate hemihydrate

3 red: Cement with 3% SO3 added as calcium sulfate hemihydrate



1 green: Cement as-is, no additional sulfate

Energy – Heat of Hydration excluding 1st h

2 yellow: Cement with 1% SO3 added as calcium sulfate hemihydrate

3 red: Cement with 3% SO3 added as calcium sulfate hemihydrate

Energy or "Heat of Hydration" correlates with compressive strength

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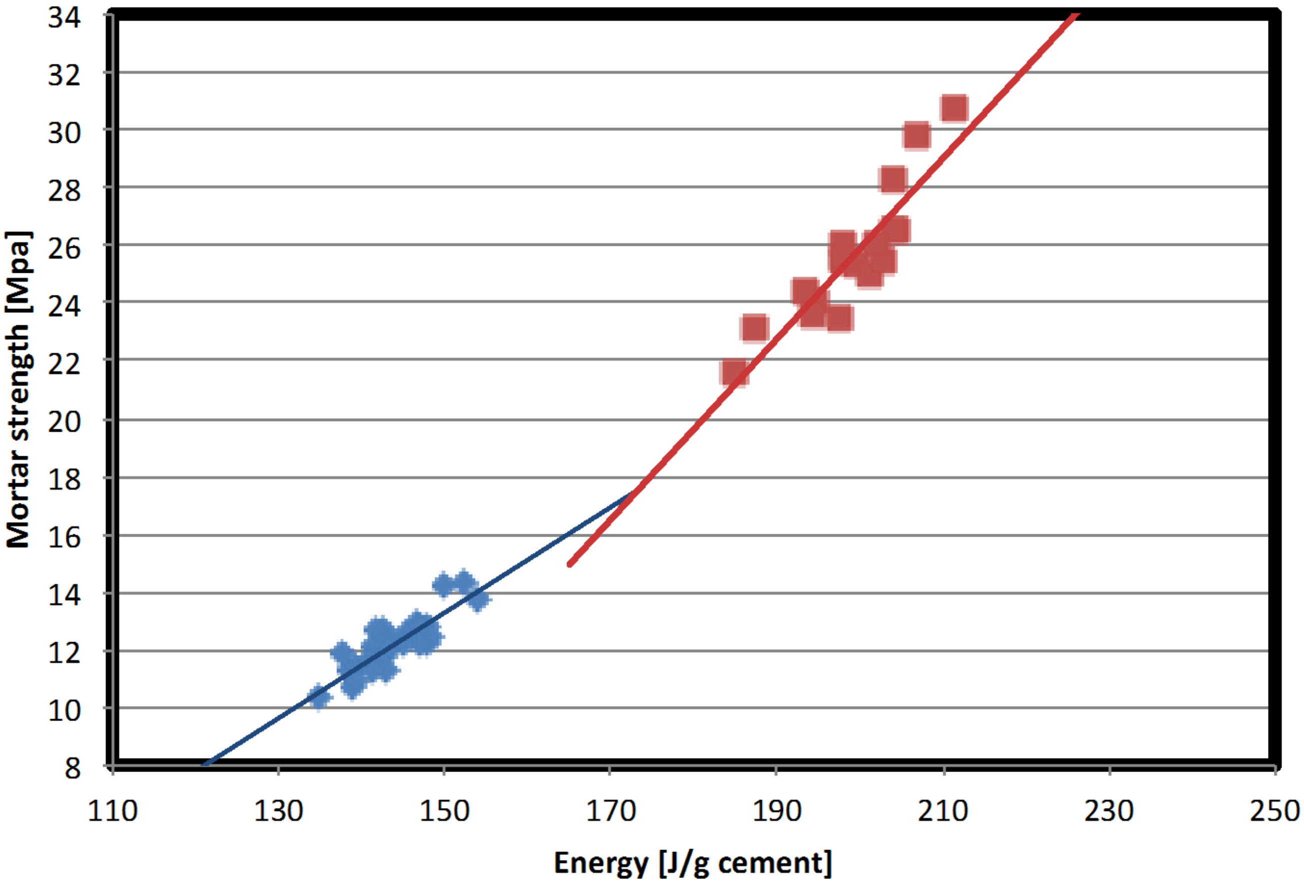
Correlation between HoH and compressive strength

Example: Relationship between HoH and 1 to 7 -day mortar strength for two different cements based on two distinctly different clinkers – study conducted by Aalborg Cement (Cementir)



Graphics & data courtesy of Aalborg Cement

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ASTM C 1702 – Heat of hydration using isothermal calorimetry

- **Heat of Hydration** is the single largest use of isothermal calorimetry in the North American Cement industry
- Other major applications include **Sulfate optimization** and **admixture compatibility**
- Several Round Robins in North America and Europe on Heat of Hydration using Isothermal calorimetry, based on early Nordtest document developed by Lars Wadso
- ASTM 2012 RR the largest with 28 labs, 4 makes of isothermal calorimeters, and 6 different cements using ASTM C1702
  - 3 portland and 3 blended cements
  - Cement paste at 23 C, w/c 0.50
  - Method A – Internal mixing 120 tests completed for 6 cements
  - Method B – external mixing 440 tests completed for 6 cements

C1702 Coefficient of variation by age and cement

ASTM C1702 2012 Repeatability CoV % within-lab for 28 cement labs, 3 commercial calorimeter types, cement paste w/c 0.5							
Age: 7 days	Cement type	ASTM II CEN I	ASTM IP CEM IIA	ASTM V CEN I SR	ASTM IS CEM III	ASTM I CEN I	ASTM IL CEN IIA/L
Heat of Hydration	internal mixing	1.2%	1.5%	1.4%	2.1%	1.0%	1.7%
ASTM C1702 isothermal	external mixing	1.2%	1.0%	1.3%	1.2%	0.7%	0.8%
calorimetry	all	1.2%	1.2%	1.3%	1.4%	0.8%	1.0%

- As in the past – excellent repeatability **within each lab**
- Internal mixing was NOT more repeatable- but difference was insignificant
- Compare with ~ 3% CoV for a good compressive strength testing lab

ASTM C1702 2012 Reproducibility CoV % between-labs for 5 cement labs, single calibration & verification before test, 7d cement paste w/c 0.5							
Pre-conditioned water	Cement type	ASTM II CEN I	ASTM IP CEM IIA	ASTM V CEN I SR	ASTM IS CEM III	ASTM I CEN I	ASTM IL CEN IIA/L
ASTM C1702	external mixing	0.9%	1.4%	1.1%	0.6%	0.3%	0.5%

- ASTM C1702 requires water to be pre-conditioned to the same temperature as the calorimeter within 0.2° C

- Further improvements through better calibration routines are possible!

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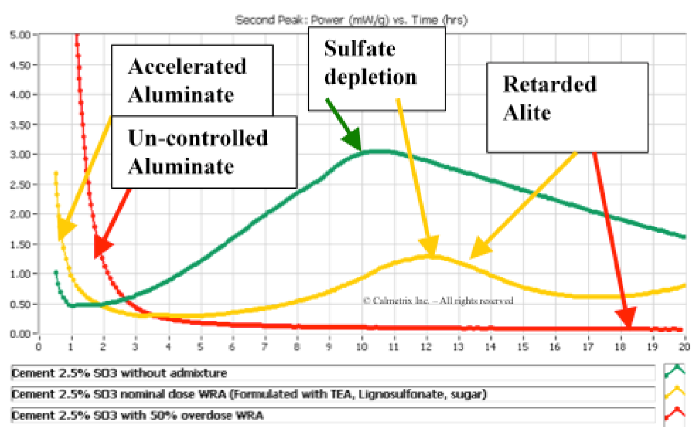
Sulfate optimization – why is it important?

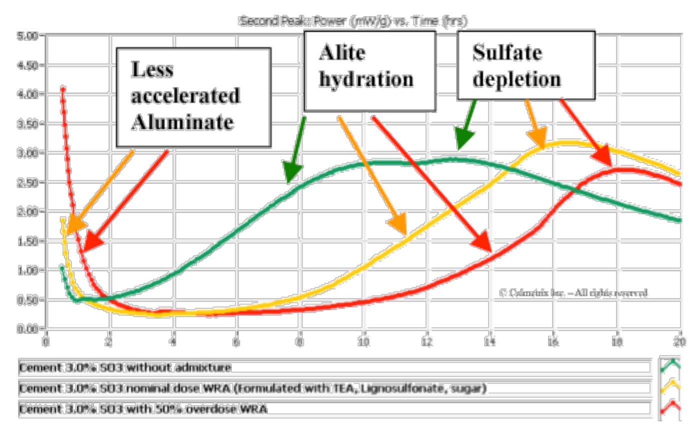
- Calcium sulfate is added to the mill to control the aluminates, which would otherwise cause premature stiffening and poor strength development

- Traditionally, the cement producer only tests cement and water, by measuring the compressive strength at different sulfate addition levels in order to find an optimum sulfate addition at a target curing age.

- The effects of admixture, SCMs and temperature is known to be very important – but are largely ignored by the cement standards.

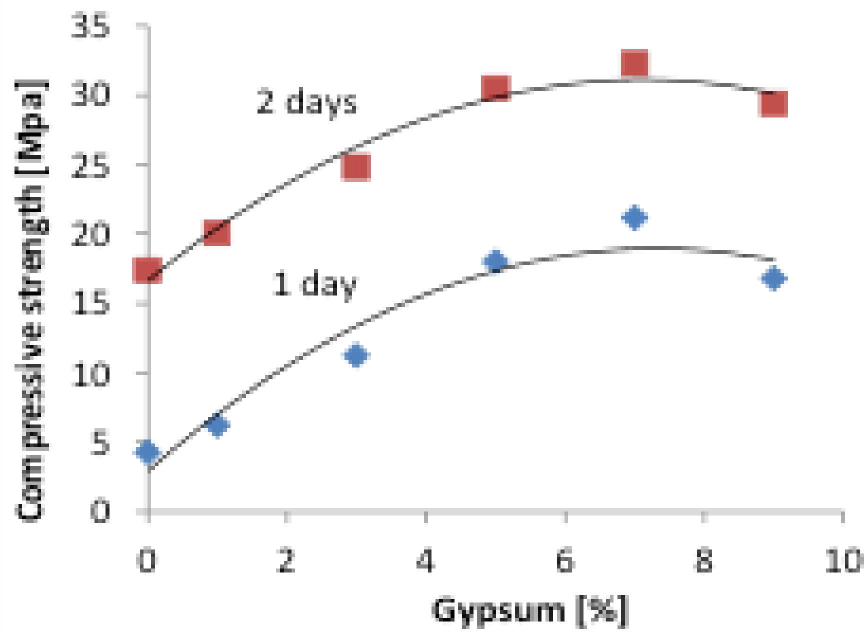
- **No air conditioned laboratory required – the isothermal calorimeter is the lab**
- **Anyone can do sulfate optimization using calorimetry with basic training**





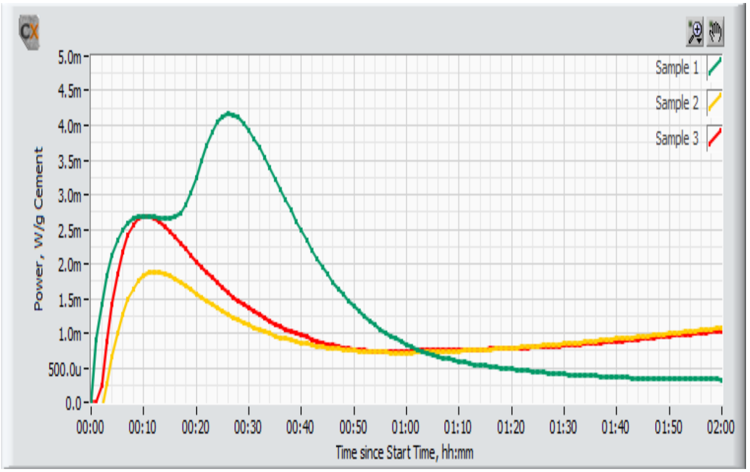
Traditional sulfate optimization using compressive strength

- Traditionally, the cement is optimized by measuring the compressive strength at different sulfate addition levels in order to find an optimum sulfate addition at a target curing age

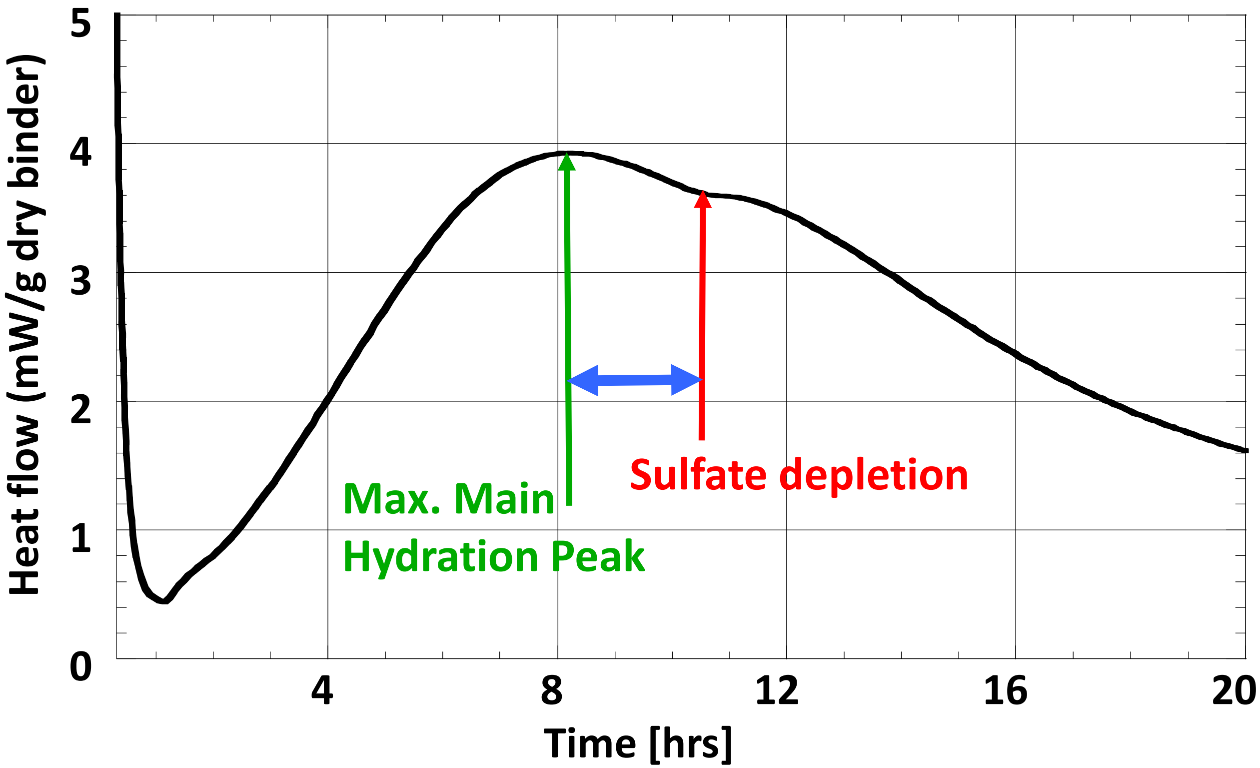


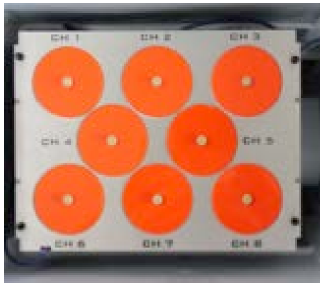
- Air conditioned lab with controlled moist curing and and compressive strength testing at precise ages – many cement plants are not equipped to do this.

- Traditional strength testing gives no information about the **sulfate balance at early age**
- **Cement could be unbalanced before set, experiencing poor workability, and still be optimized for compressive strength development**



“Sulfate Depletion Peak” method





- Visually simple, provided that the depletion peak does not completely overlap with the alite hydration peak
- For a given cement and test condition define the target time elapsed from the maximum of the main peak and the beginning of the sulfate depletion peak
- Most isothermal calorimeters will work very well for the “sulfate depletion peak” method

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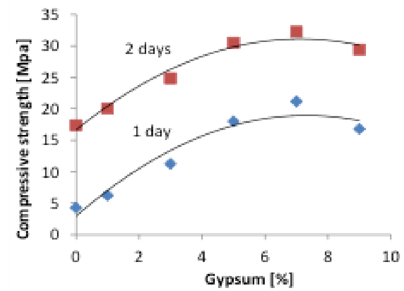
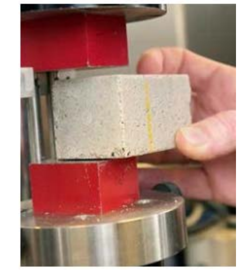
Step 1 – Define sulfate optimum

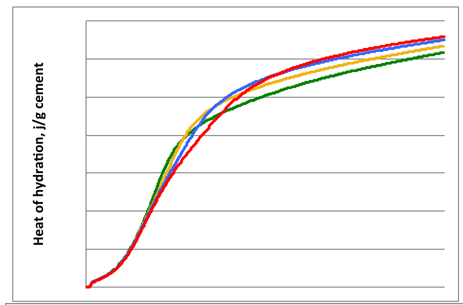
- **Traditional compressive strength – lab needed**



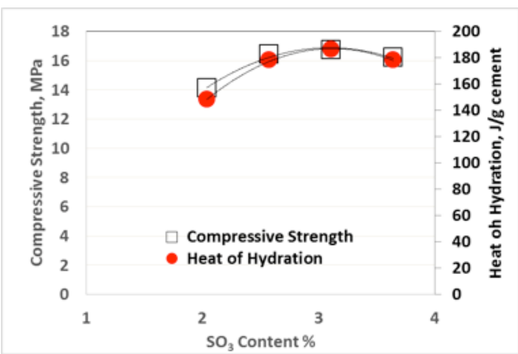


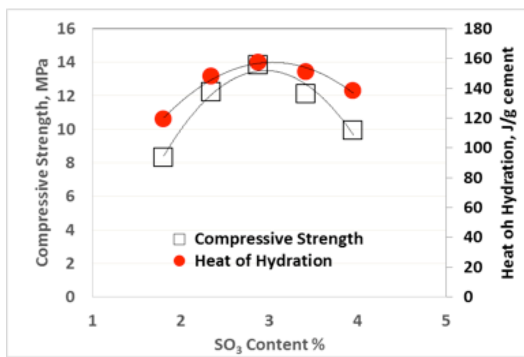
OR

- **New: Isothermal calorimetry Heat of Hydration**



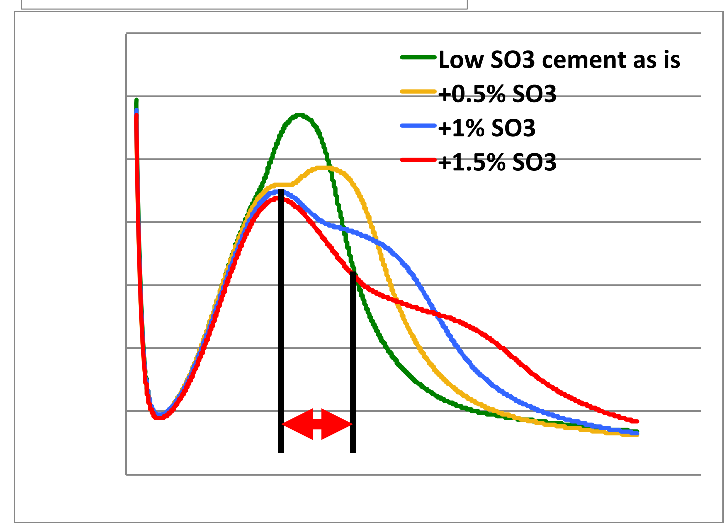
- Correlates very well with compressive strength





CEM II/A-W	ASTM T-IP

CEM II/A-L	ASTM T-IL



- **Define time between maximum of main peak to sulfate depletion**
- At maximum Heat of Hydration or compressive strength at desired age(s)

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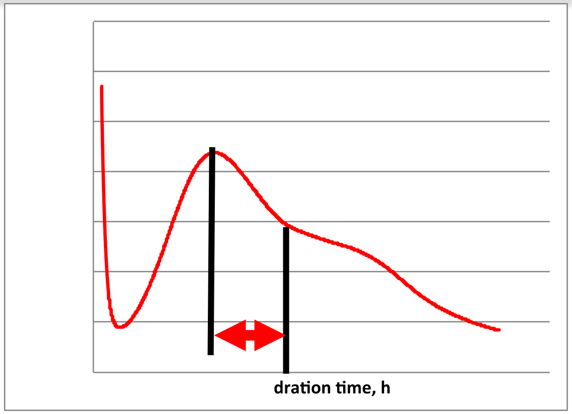
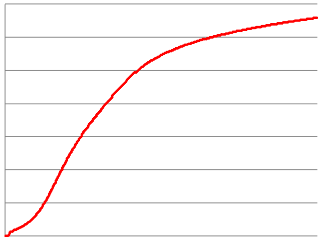
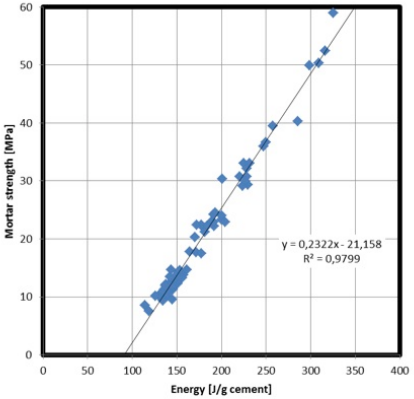
Step 2 – Continuous QC calorimetry on finished cement



- **Time from main peak max to sulfate depletion**

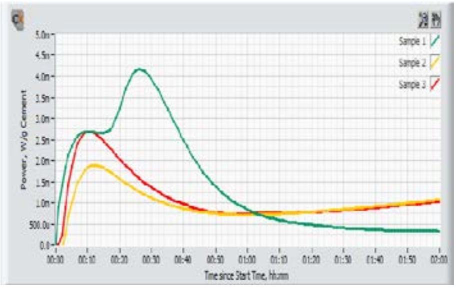




- **Heat of Hydration**
- Excellent strength prediction

Optimum SO3 at optimum time between main peak max and sulfate depletion
Best correlation between HoH and strength
Maximum strength

- **Optionally analyze initial peak for abnormal aluminate hydration**
- Alkali-sulfate balance in kiln, ortho C3A etc



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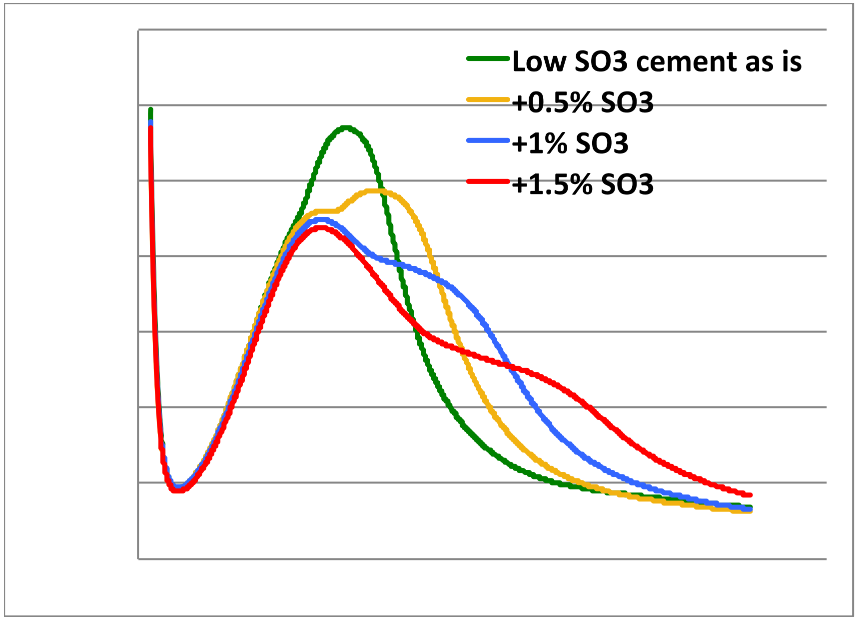
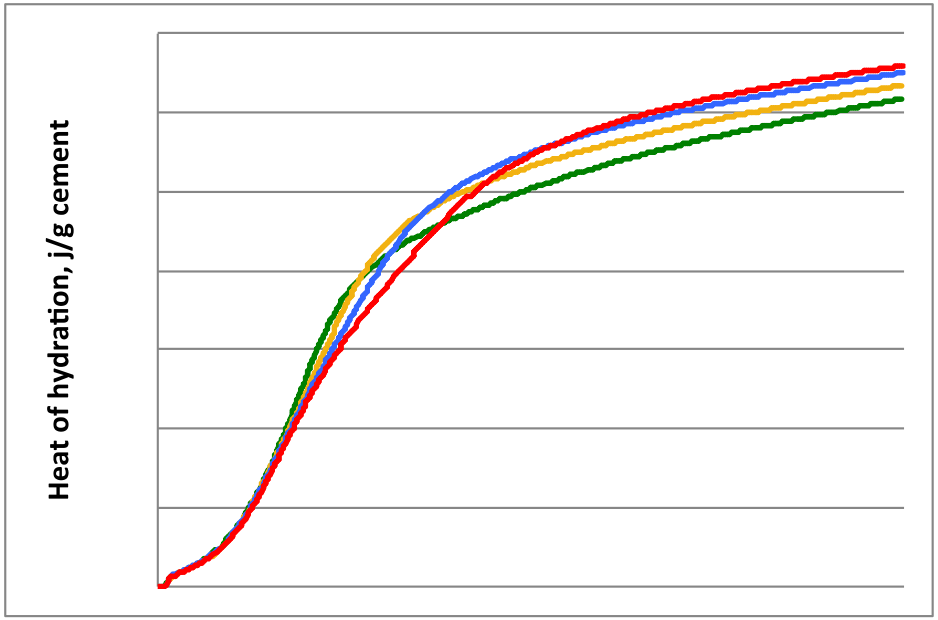
Defining and QC optimum SO3 using isothermal calorimetry





Summary sulfate optimization

- Heat of Hydration by isothermal calorimetry is an excellent alternative to compressive strength testing when testing for optimum SO3.
- No lab or AC is required since the calorimeter itself is the "lab"
- Can easily test for the effect of temperature, admixtures, SCM, etc.
- If the 1st hour gives noisy data, depending on sample preparation method and calorimeter used, then accuracy is improved by eliminating the heat from the 1st hour

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Temperature effects on cement hydration

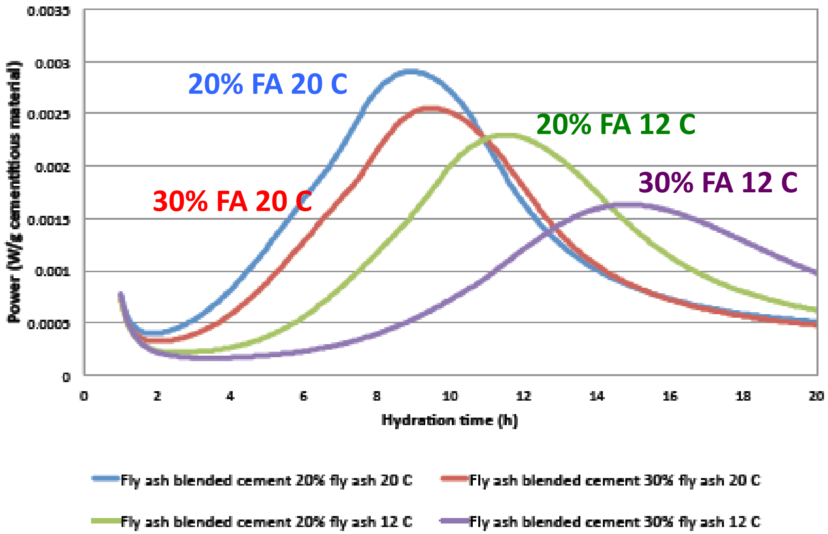


Figure 5: effect of temperature on the hydration profile for a fly ash blended cement, power or heat flow (reaction rate). One may infer an indication of relative effects on setting time by comparing the time to reach half of the maximum power. Thus the effect of increasing fly ash content from 20 to 30 per cent in this example is less than an hour at 20˚C but more than 2h at 12˚C

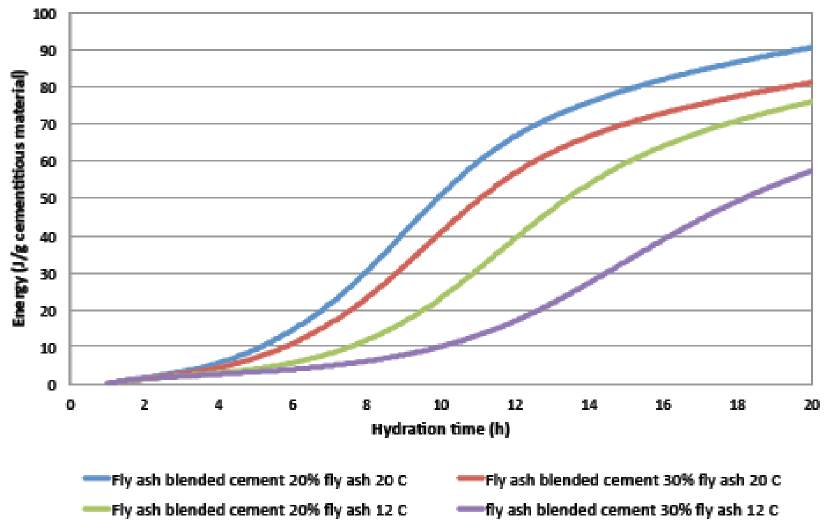
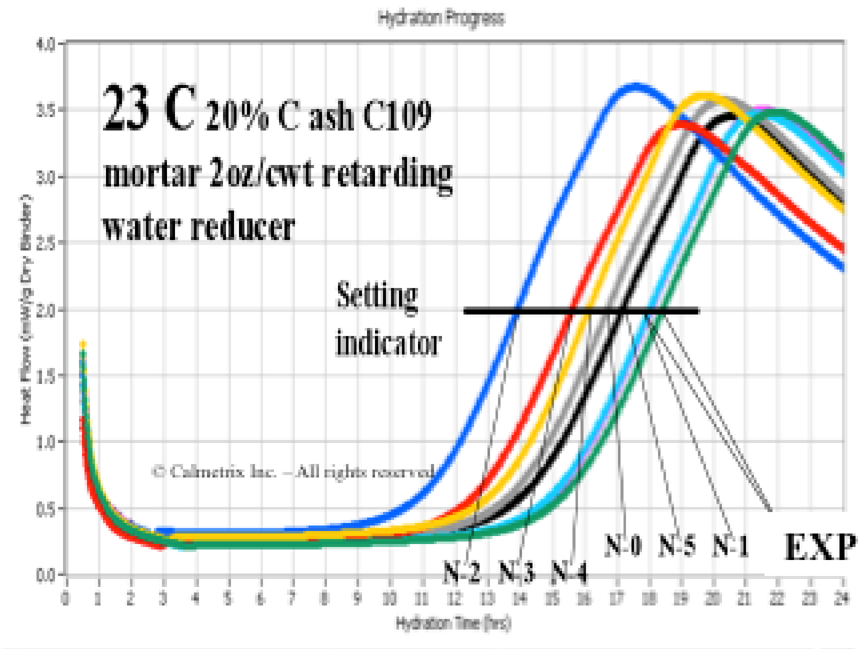
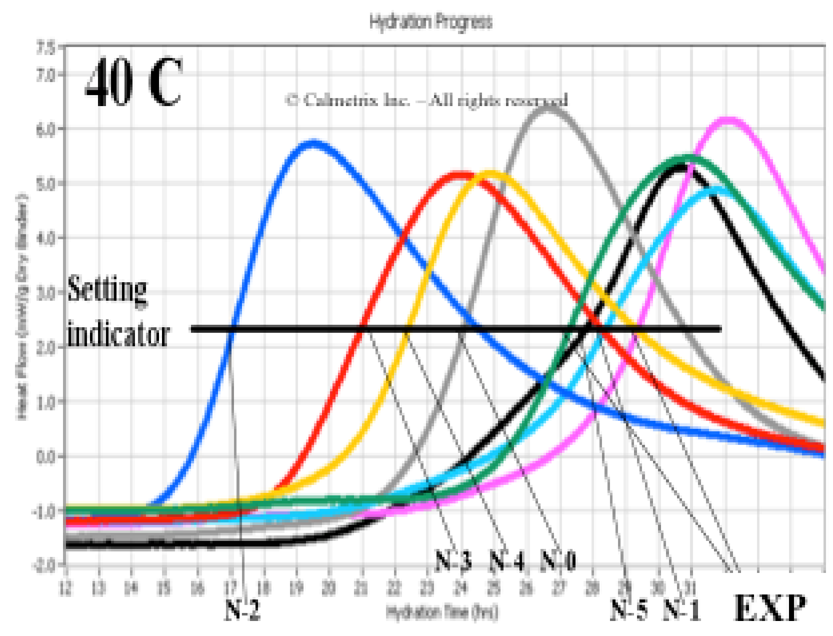


Figure 6: effect of temperature on the hydration profile for a fly ash blended cement, Energy or Heat of Hydration ("degree of hydration"). One may infer an indication of relative effects on strength development by comparing the heat of hydration at a given hydration time. Thus the effect of increasing fly ash content from 20 to 30 per cent in this example at 18h is approximately 15 per cent strength loss at 20°C and ~30 per cent strength loss at 12˚C

Admixture – Non-Linearity with Temperature



20% C Ash, 130 mL/100 kg Type A water reducer



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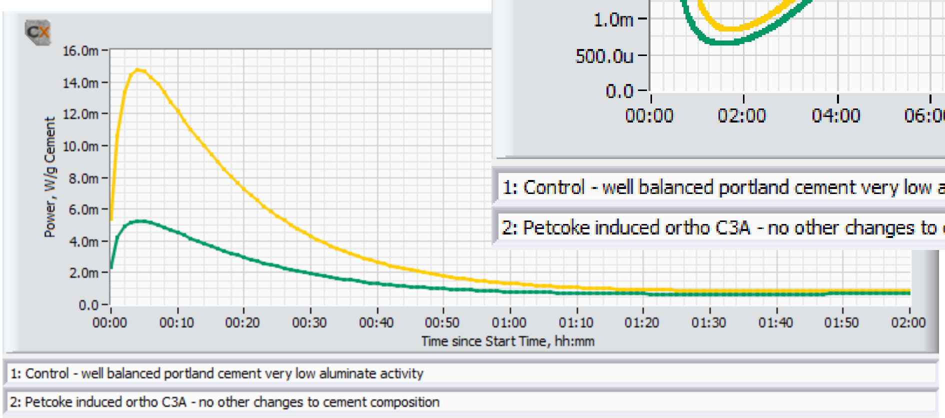
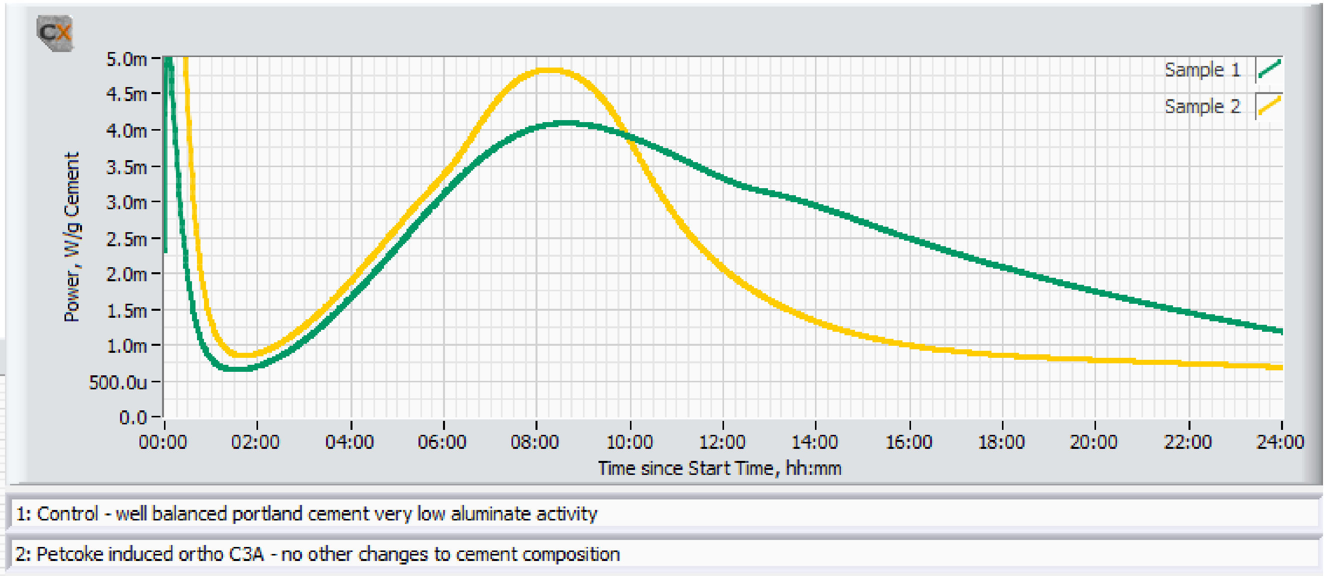
Early stiffening - An example of uncontrolled aluminate

- Industrial clinker was produced using fixed raw materials and raw meal composition **except** for the type of fuel
- Types and amounts of secondary fuels were used to reduce dependency on traditional fossil fuels
- Clinkers were ground to a constant fineness in conjunction with different sulfate forms added to the laboratory mill
- Example shows calorimetry of clinker with increase use of pet coke – a common case in the industry
- All clinkers were ground with calcium sulfate to a "base" 3.0% SO3 level





- Over a certain threshold, the petcoke introduced the formation of orthorhombic C3A, causing high early reactivity and slump loss (left), and premature sulfate depletion (right)

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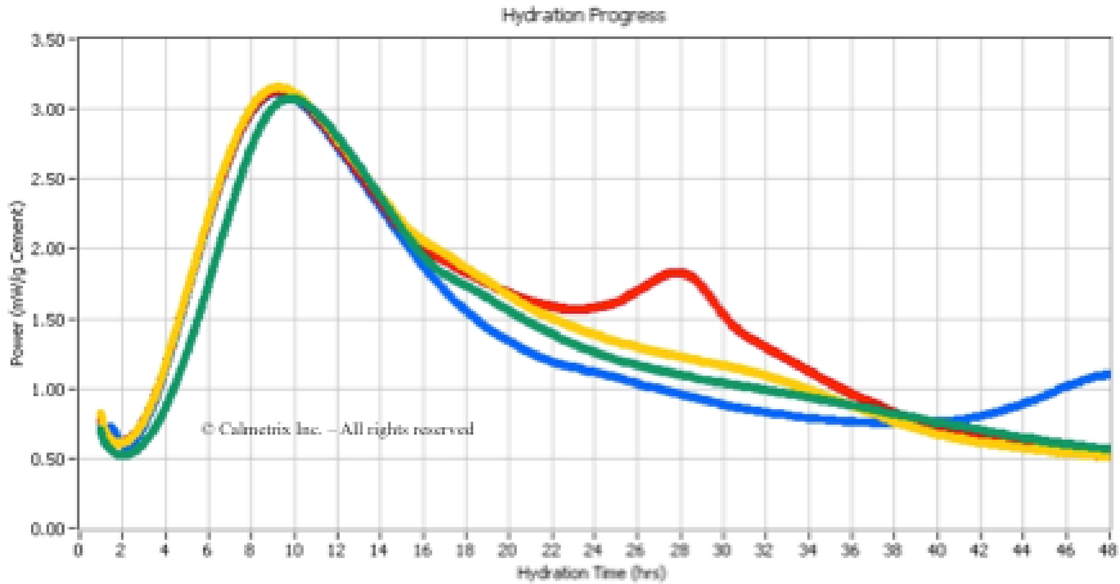
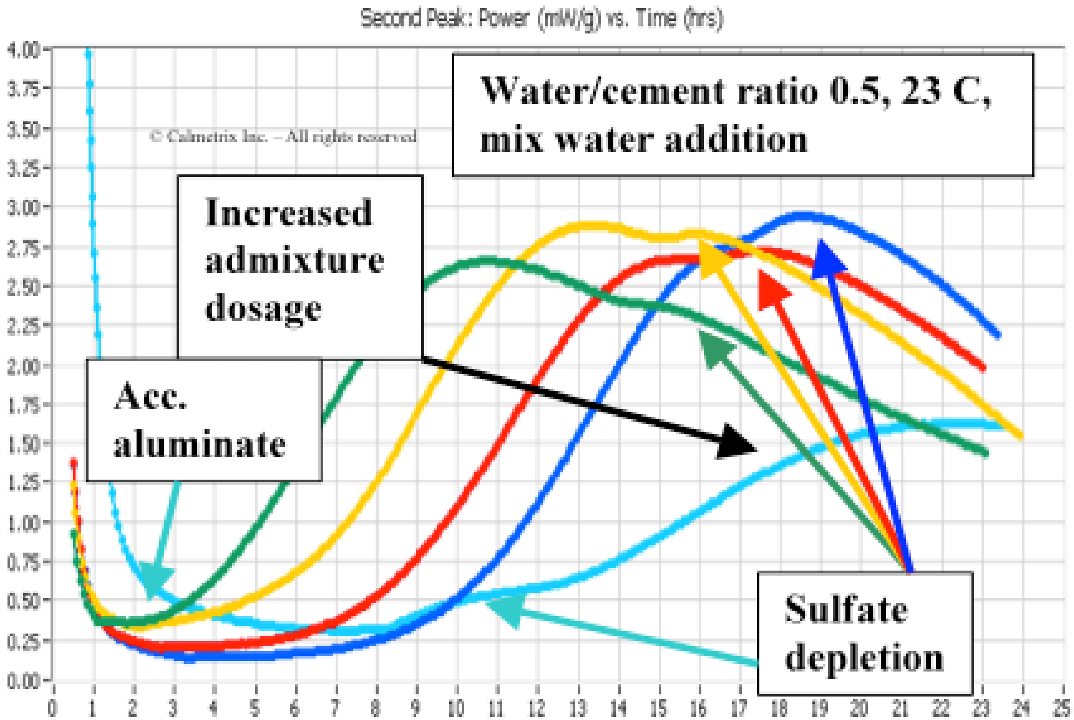
Isothermal Calorimetry to Examine Additive Effect

- **Detection of something significant**
- **Red cement additive promotes carboaluminate**
- **But does not indicate what exactly is happening**
- **Very little effect on initial silicate peak**
- **Fact that third peak moved out in time with added SO_3 indicates it is aluminate**



Green – No additive
Yellow + 20% limestone
Red - + 20% limestone plus 200 ppm TIPA
Blue - + 20% limestone plus 200 ppm TIPA + 0.5% SO_3

A typical dosage ramp of a water reducer in mortar or concrete



Green is blank (no admixture)

Yellow, red, dark blue are mixes in balance

•Red is target. Overdose, light blue tested to see how close mix is to abnormal retardation of Alite

Concrete or mortar – careful with paste, unless for mechanistic research

QUESTIONS ?

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