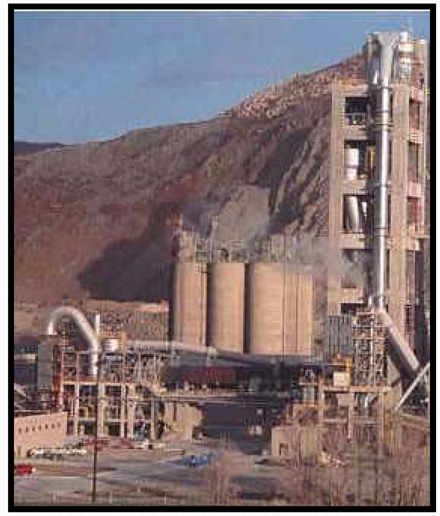
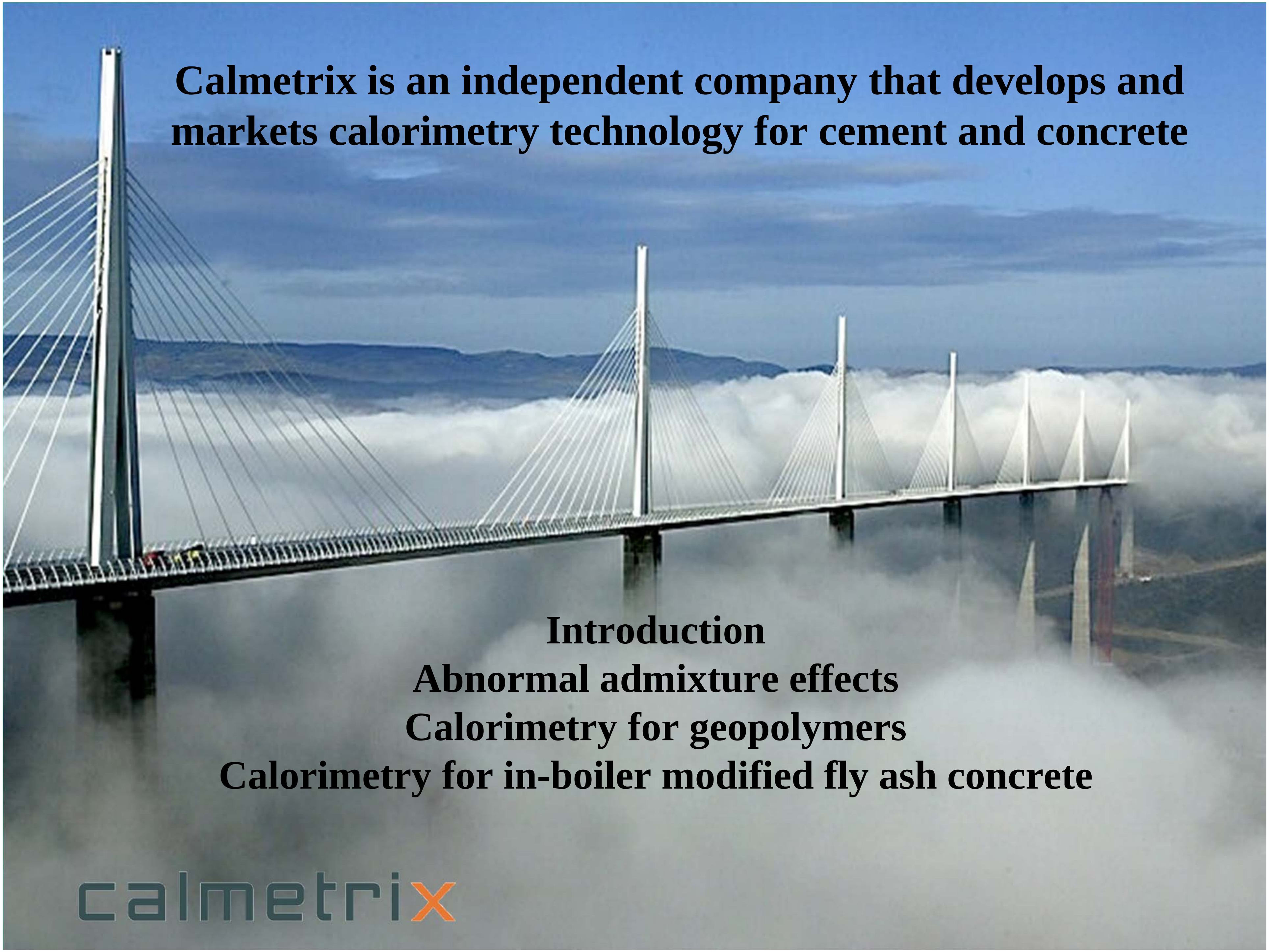


Binder – Admixture Interactions investigated using calorimetry

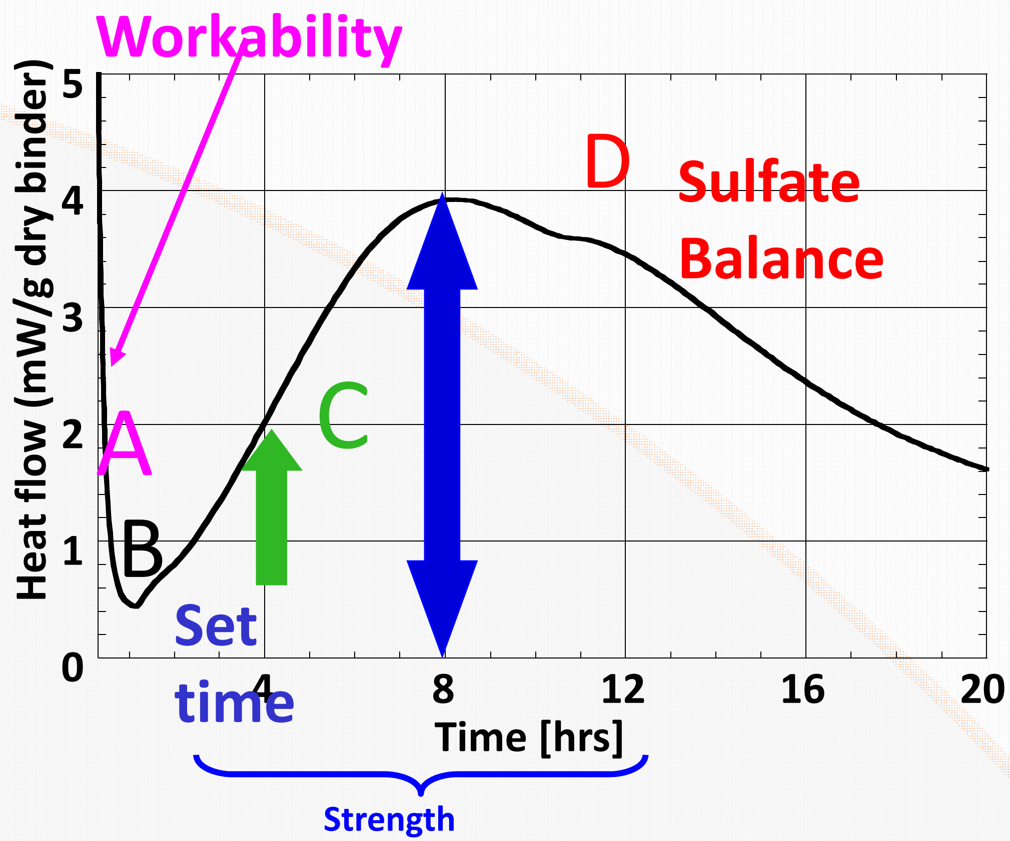
Paul Sandberg, Calmetrix & AIT


Calmetrix is an independent company that develops and markets calorimetry technology for cement and concrete
Introduction
Abnormal admixture effects
Calorimetry for geopolymers
Calorimetry for in-boiler modified fly ash concrete
calmetrix

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

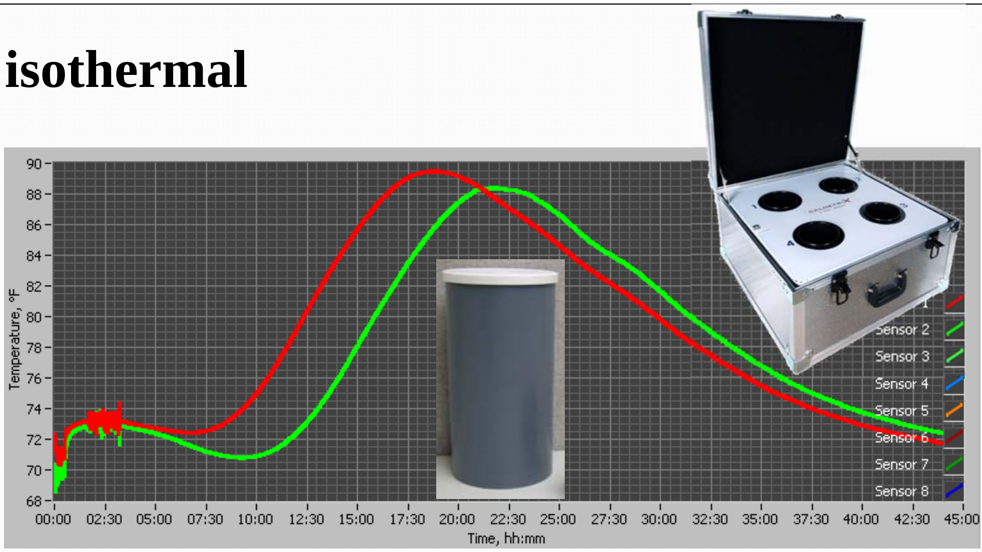


Interpretation of a calorimetry curve gives information about:

- Workability
- Setting time
- Strength gain
- Material incompatibility

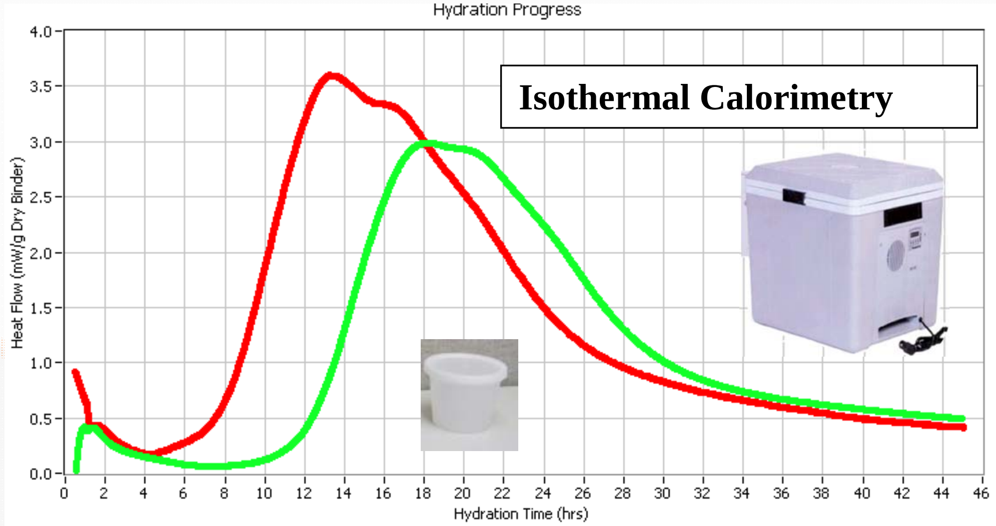
Calorimetry: Semi-adiabatic v.s isothermal

- **The Semi-adiabatic calorimeter measures a temperature rise in partially insulated concrete**
- **The isothermal calorimeter measures heat flow from the sample to a heat sensor at close to constant temperature (± 0.5 ºC or better)**



Red: 6 oz/cwt Adva 190

Green: 6 oz/cwt Adva 190 + 2 oz/cwt D17



Sample sizes	Semi-adiabatic	Isothermal
Paste	200-500 g	10-20 g
Mortar	500-1000 g	35-130 g
Concrete	4000 g	340 g

- **Example shows two concrete mixtures tested both isothermally and in the semi-adiabatic calorimeter**

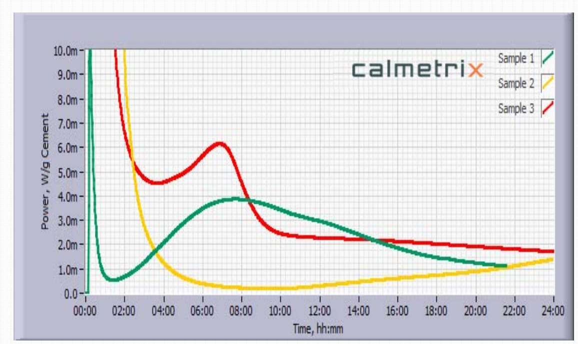
Uses of calorimetry: R&D and Quality Control

Calorimetry is like taking the Blood Pressure of Concrete

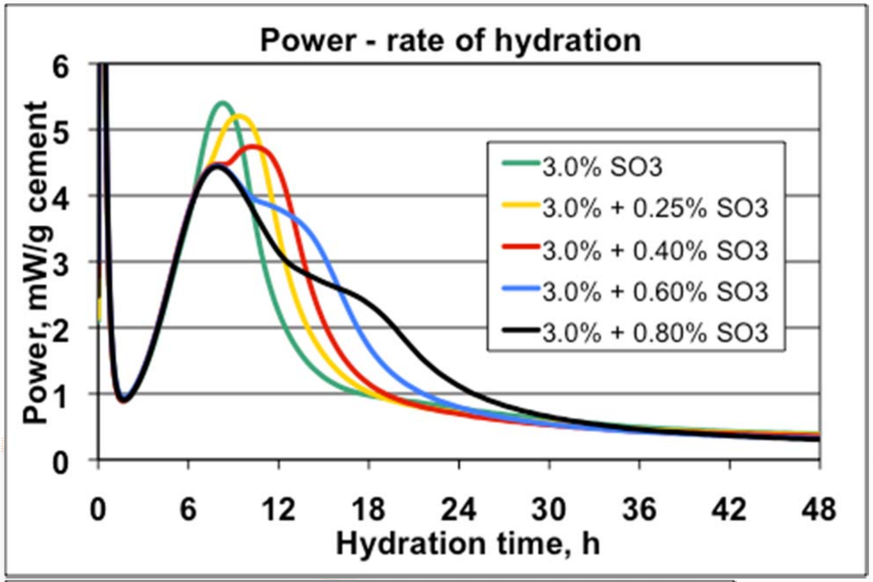
- Simple Low cost method for measuring the rate of cement hydration.
- Level of Hydration will determine rate of set and strength development.
- Used to measure effects of material and mix design on heat evolution
- Not to characterize the issues related to heat evolution

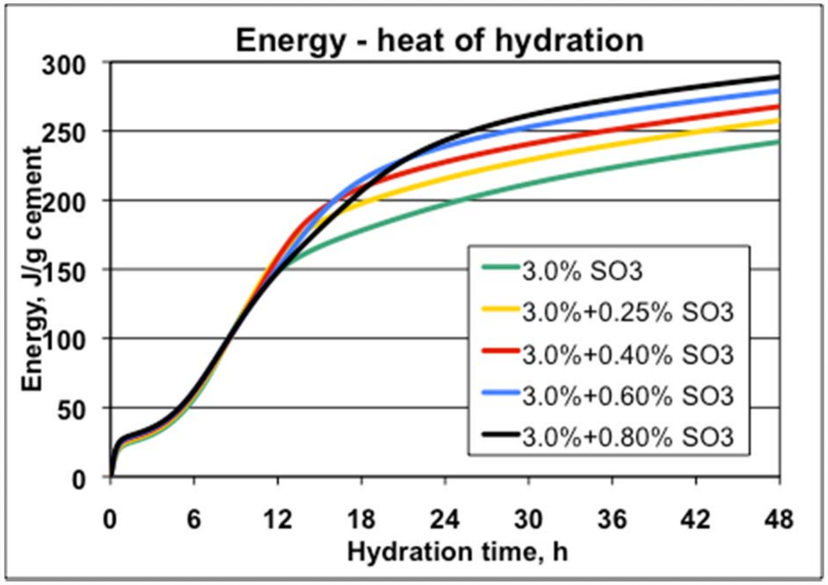
Calorimetry is a state of the art, user friendly, tool used on a daily basis in Concrete Production QC to:

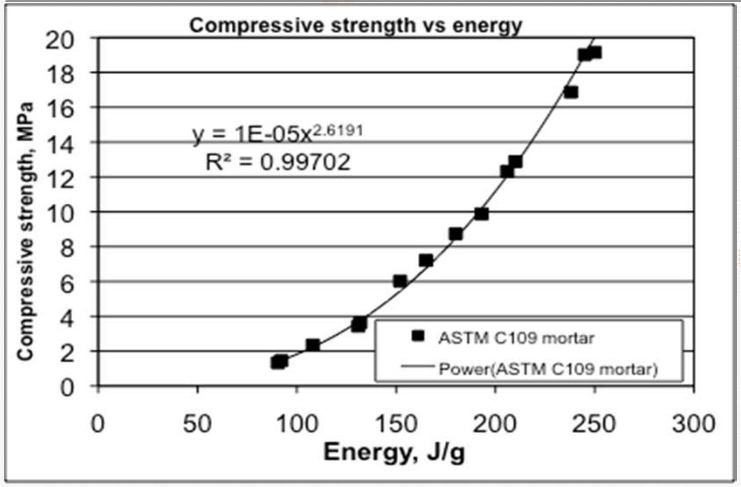
- Compare materials such as cement, Fly Ash, admixtures, etc.
- Optimize mix designs
- Troubleshoot – search for performance limits
- Control and adjust for raw material variability



“Classic” calorimetry – sulfate balance with & without admix – ASTM C1679







Energy as a proxy for degree of hydration

Strength – Energy correlation… works for a given mix design

Adding SO3 below optimum may increase ratio of aluminate sulfate hydrates vs CHS, thereby slightly altering the strength-energy correlation

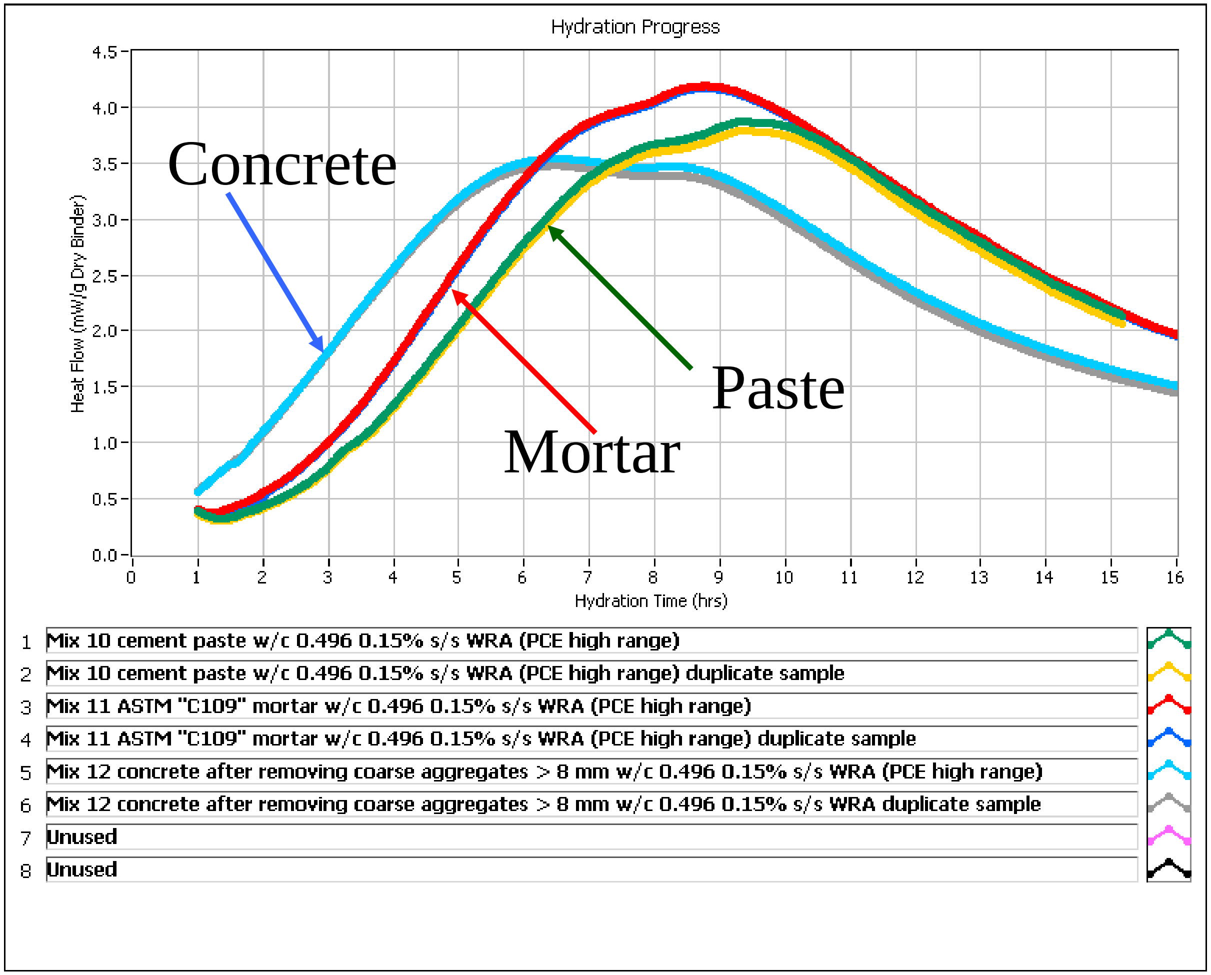
Adding or changing admixture typically does not noticeably change the strength-energy correlation after set, it just changes the timing!

Example of effect of mixing energy with Polycarboxylates

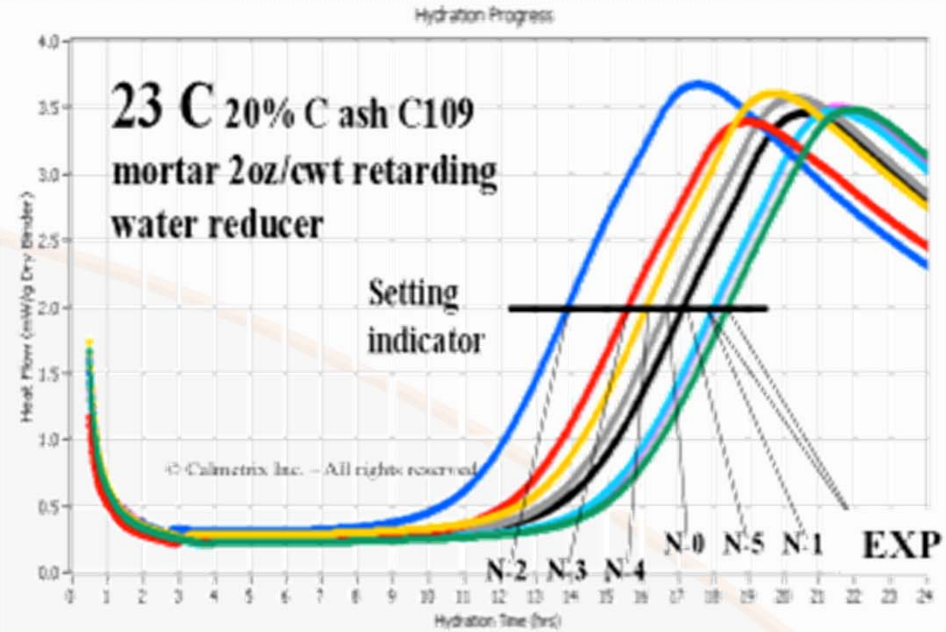
- **Replication with paste, mortar and concrete**
- **Substantially longer "set" in examples with paste**
- **Only one example – illustrative of care needed.**

See also "Evaluating the Effect of Mixing Method on Cement Hydration in the Presence of a Polycarboxylate High-Range Water Reducing Admixture by Isothermal Conduction Calorimetry" by S.A. Farrington,

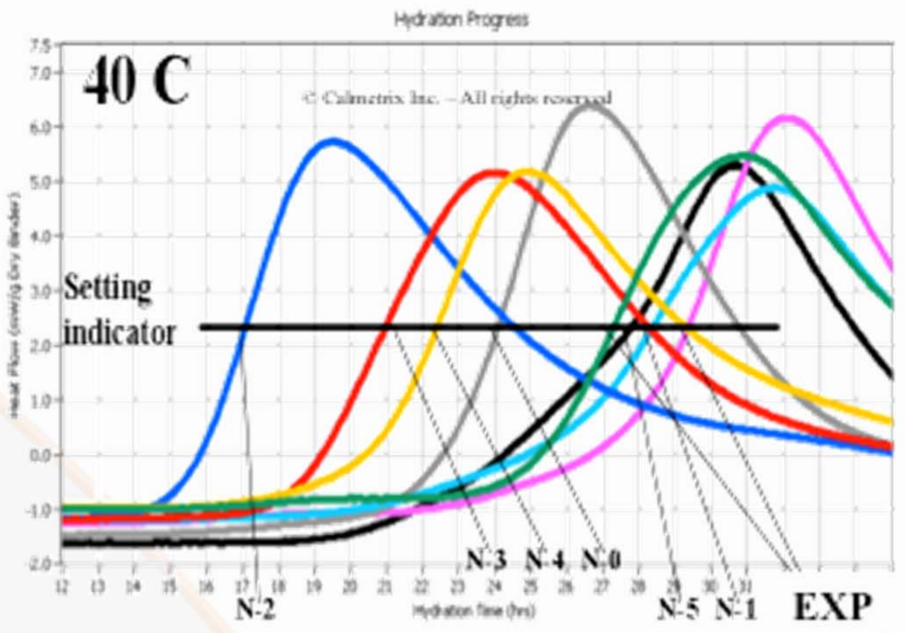
ICCC Montreal 2007



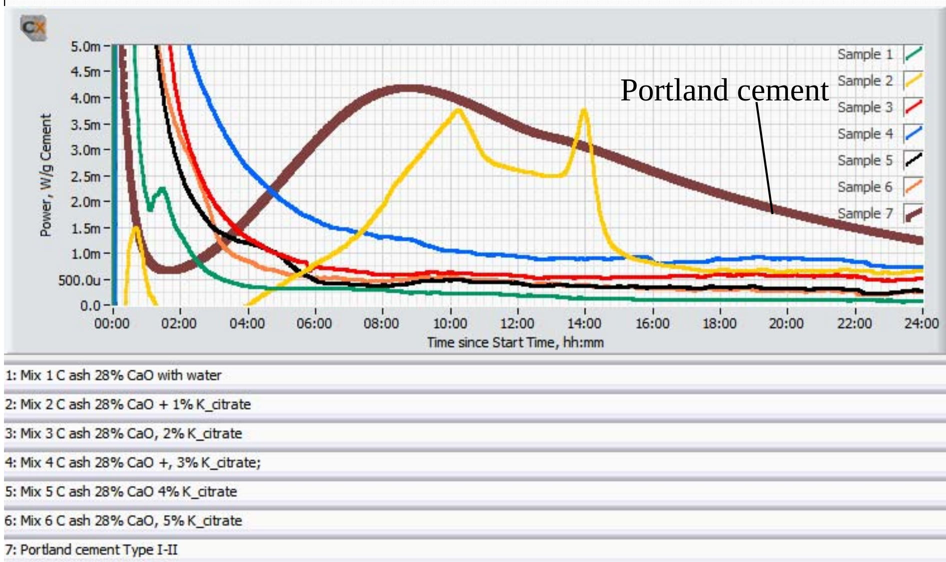
Admixture – Non-Linearity with Temperature

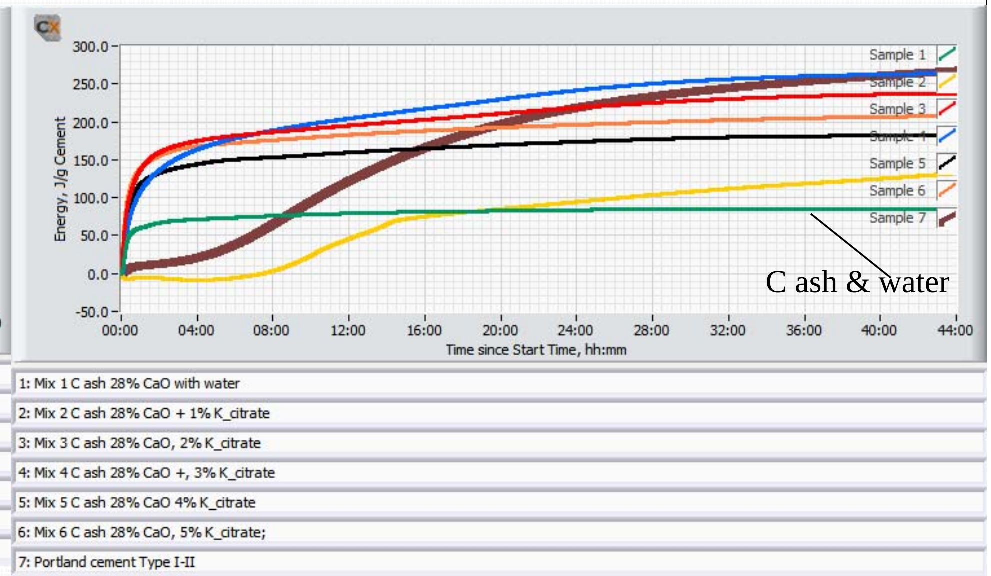


20% C Ash, 130 mL/100 kg
Type A water reducer



Geopolymer – calorimetry for rapid fly ash & admix screening





Power – Speed of reaction   Energy – Heat of reaction

Accelerator dosing ramp. 1-5% potassium citrate

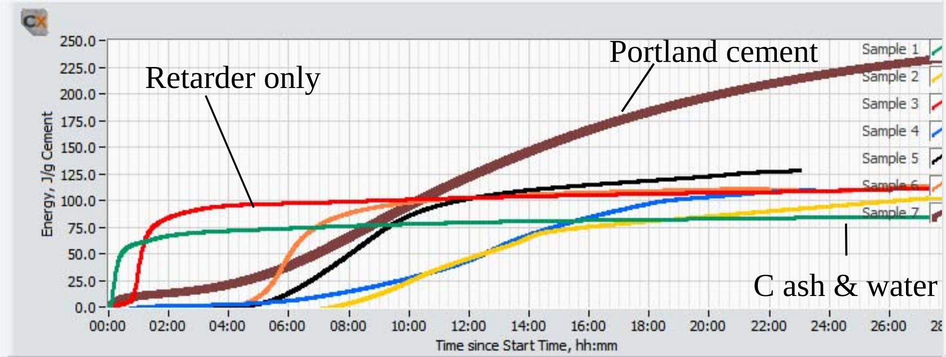
Energy ~ Degree of reaction

Each fly ash may react very differently to each chemical

Avoid surprises … parameters and material inputs change when placing concrete in the field. Use Calorimetry to Screen for sensitivity of a mixture to changes.

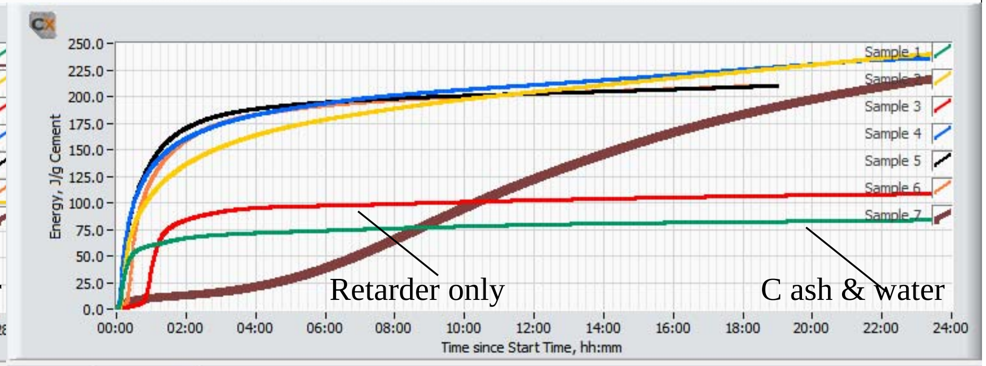
See US patent # 8016937(Ceratech) for details on citrate as a C ash activator

Geopolymer – calorimetry for rapid fly ash & admix screening



1:green C ash 28% CaO with water
2: yellow C ash 28% CaO + 1% K_citrate
3:red C ash 28% CaO + 0,4% Borax
4:blue C ash 28% CaO + 1% K-citrate + 0,4% Borax
5: black C ash 28% CaO + 1% K-citrate + 0,8% Borax
6: orange C ash 28% CaO + 1% K-citrate + 1,2% Borax
7:thick brown Portland cement Type I-II

1% accelerator



1: green C ash 28% CaO with water
2: yellow C ash 28% CaO +, 3% K_citrate
3: red C ash 28% CaO + 0,4% Borax
4: blue C ash 28% CaO + 3% K-citrate + 0,4% Borax
5: black C ash 28% CaO + 3% K-citrate + 0,8% Borax
6: orange C ash 28% CaO + 3% K-citrate + 1,2% Borax
7: thick brown Portland cement Type I-II

3% accelerator

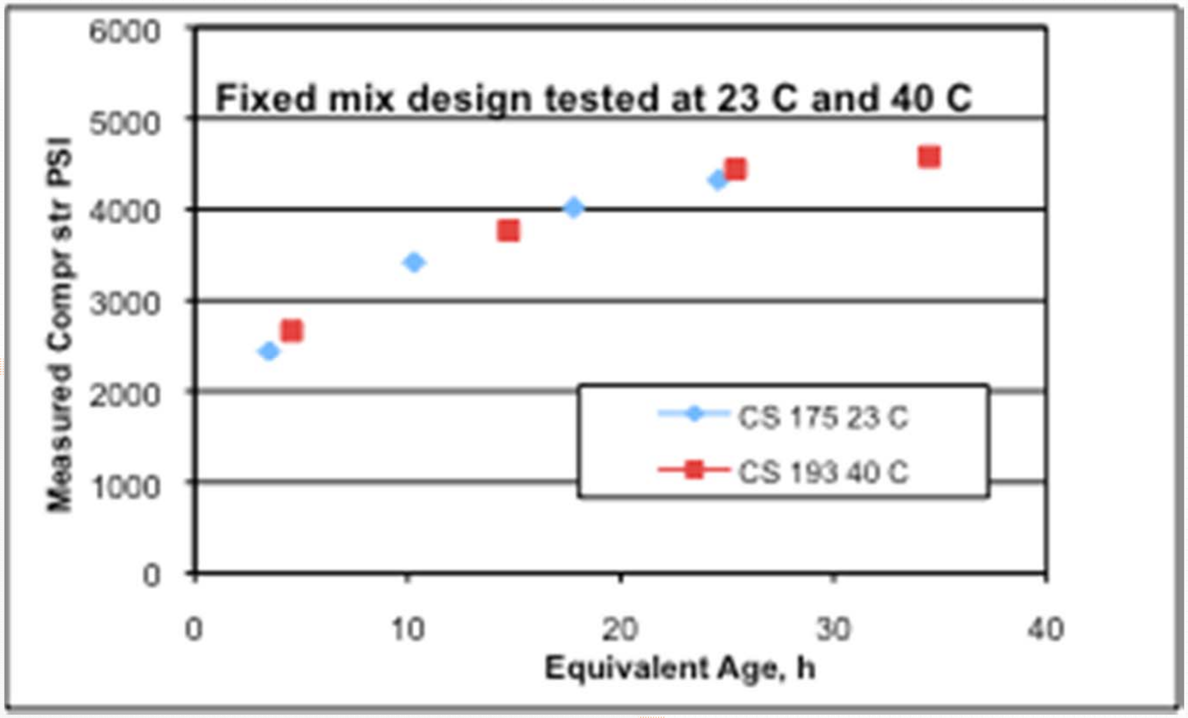
1% or 3% accelerator with retarder.

This ash needs ~ 3% accelerator for high early strength. Easy to "dial-in" right amount of retarder.

Each fly ash may react very differently to each chemical

Avoid surprises … parameters and material inputs change when placing concrete in the field. Use Calorimetry to Screen for sensitivity of a mixture to changes. Fly ash batch-to-batch variations can be significant!!!

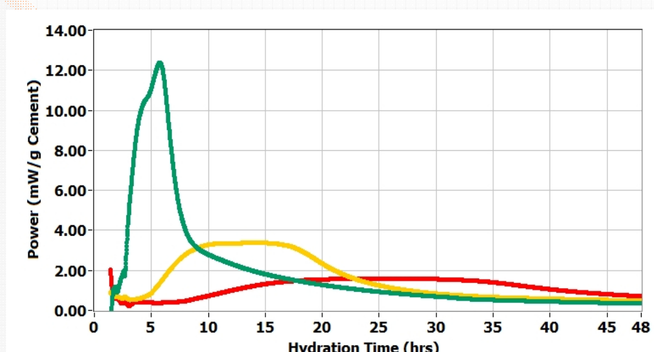
Can calorimetry (temperature history or heat of hydration) be used to predict compressive strength?

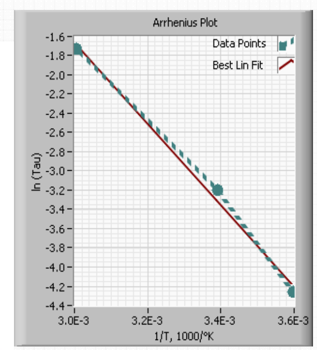


Example shows concrete in semi-adiabatic calorimeter. Can also be done using isothermal calorimeter, using heat of hydration as a proxy for degree of hydration

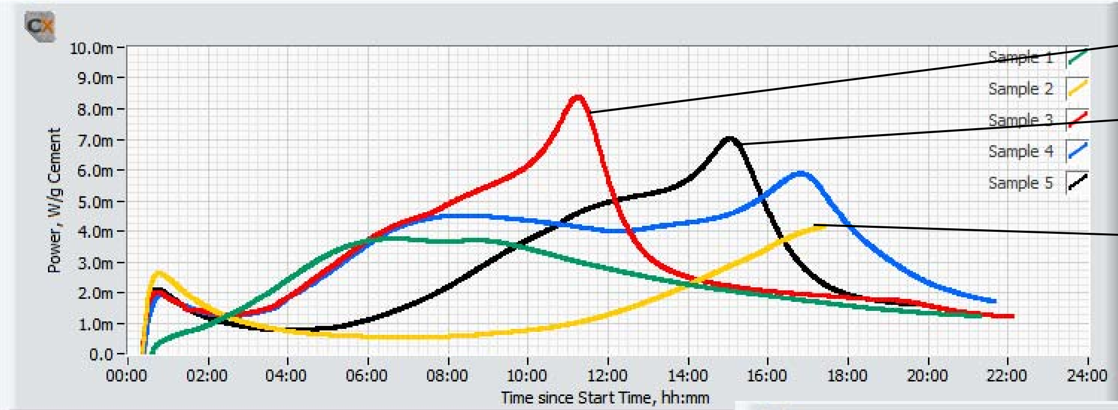
Calorimetry / Maturity does seem to work for a given C ash activated with potassium citrate.

Avoid surprises … Maturity does not always work! Maturity requires that temperature only changes the rate of reaction, not the overall path (compare with CA cement)





Class C ash often retards set in HVFA concrete



1: green Portland cement with water

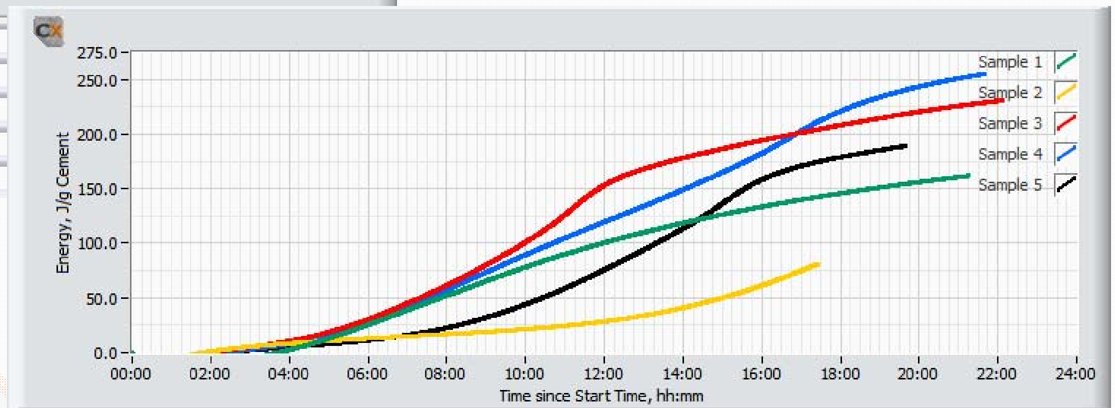
2: yellow Portland cement 50% replaced with C ash, no admixture

3: red 50% C ash + new non chloride acceleraor 20 minutes delayed addition

4: blue 50% C ash + new accelerator delayed + 2% gypsum

5: black 50% C ash + new non chloride accelerator upfront addition

Power – Speed of reaction



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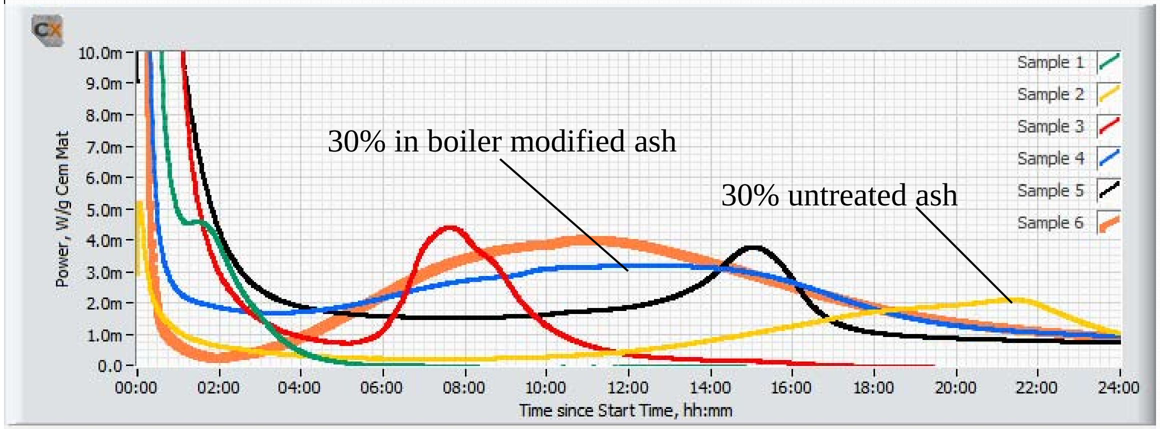
Energy – Heat of reaction

Graphs show Power and Energy by weight of portland cement.

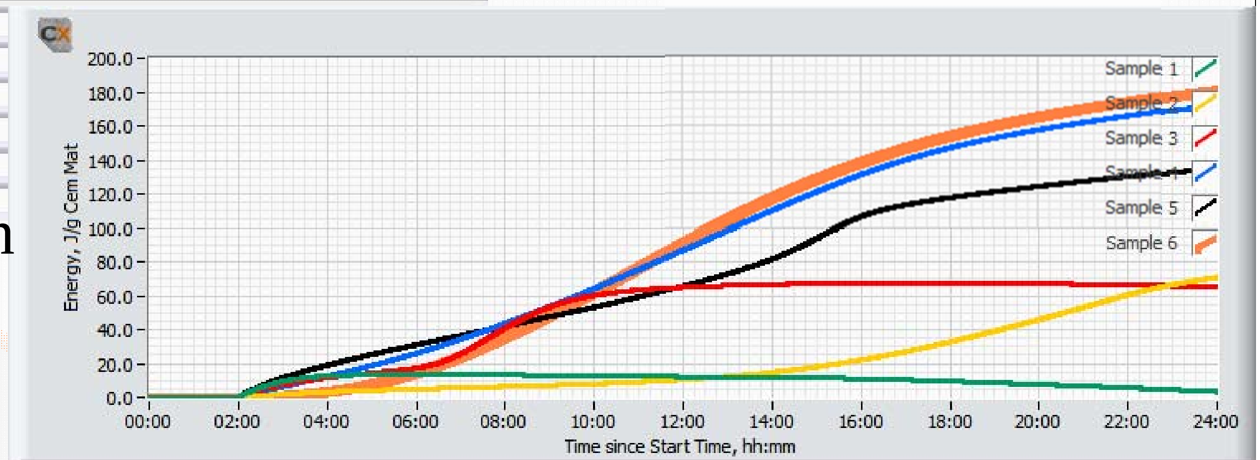
Note how the admixture accelerates the overall heat well beyond that of a 100% portland mix, meaning the admixture works directly on hydration of the C ash.

In-boiler modified ash can accelerate both set and strength gain



1 green: 100% Untreated C ash
2 yellow: Portland cement with 30% untreated C ash
3 red: 100% In-boiler modified C ash
4 blue: Portland cement with 30% in-boiler modified C ash
5 black: Portland cement with 60% in-boiler modified C ash
6 thick orange: 100% portland cement

Power – Speed of reaction



1 green: 100% Untreated C ash
2 yellow: Portland cement with 30% un-modified C ash
3 red: 100% In-boiler modified C ash
4 blue: Portland cement with 30% in-boiler modified C ash
5 black: Portland cement with 60% in-boiler modified C ash
6 orange: 100% portland cement

Energy – Heat of reaction

1-day strength with 30% in-boiler modified ash was 35% higher than 100% portland

- And 60% in-boiler modified ash outperforms 30% untreated ash