Sulfate optimization of cement using Isothermal calorimetry

Paul Sandberg

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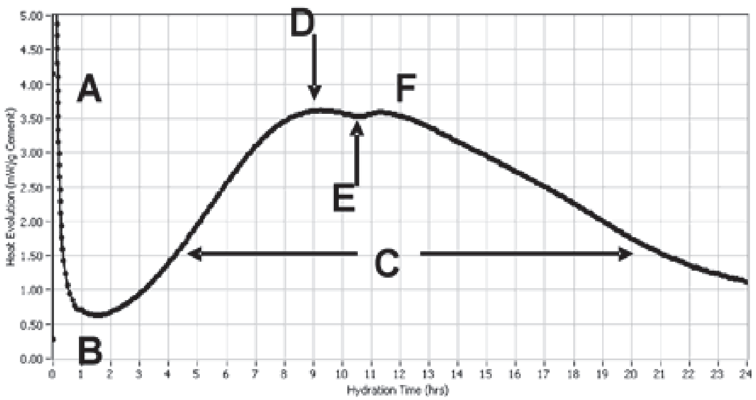
Sulfate optimization – why is it important?

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

- Proper aluminate control of Portland based cements means that ***sulfate depletion (E) only happens well after the maximum of the alite hydration (D)***



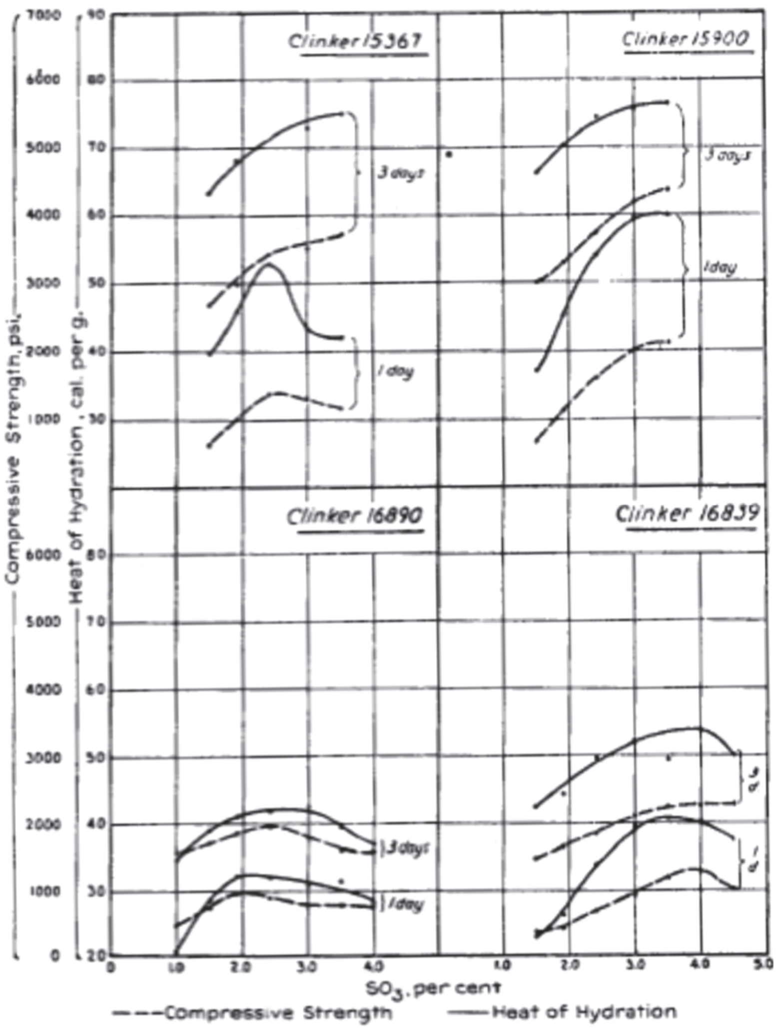
- Traditionally, the cement producer only tests cement and water, by measuring the compressive strength at different sulfate addition levels in order to find an optimum sulfate addition at a target curing age.

- The effects of admixture, temperature and additional SCM's are very important – but largely ignored by the cement standards with the exception of ASTM C563.

- **Consistent strength development and workability at sulfate optimum**
- **Normal process variability has less impact on performance at optimum**

Lerch's classic paper in 1946 set the stage for isothermal cement calorimetry

LERCH ON INFLUENCE OF GYPSUM ON PORTLAND CEMENT PAS



8.—Relationship Between Heats of Hydration and Compressive Strengths at Early Ages.

20 LERCH ON INFLUENCE OF GYPSUM ON PORTLAND CEMENT PASTES

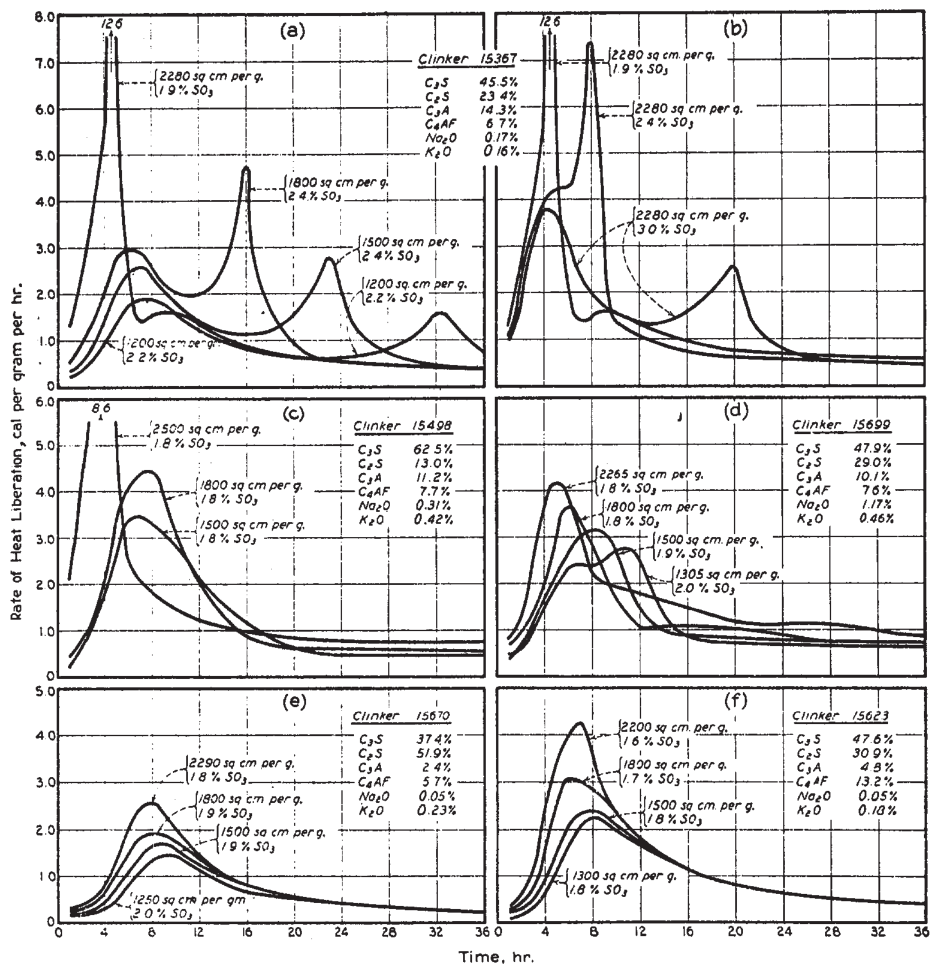


FIG. 14.—Effect of Specific Surface Upon the Heat of Hydration.

Applicable for modern blended cements?

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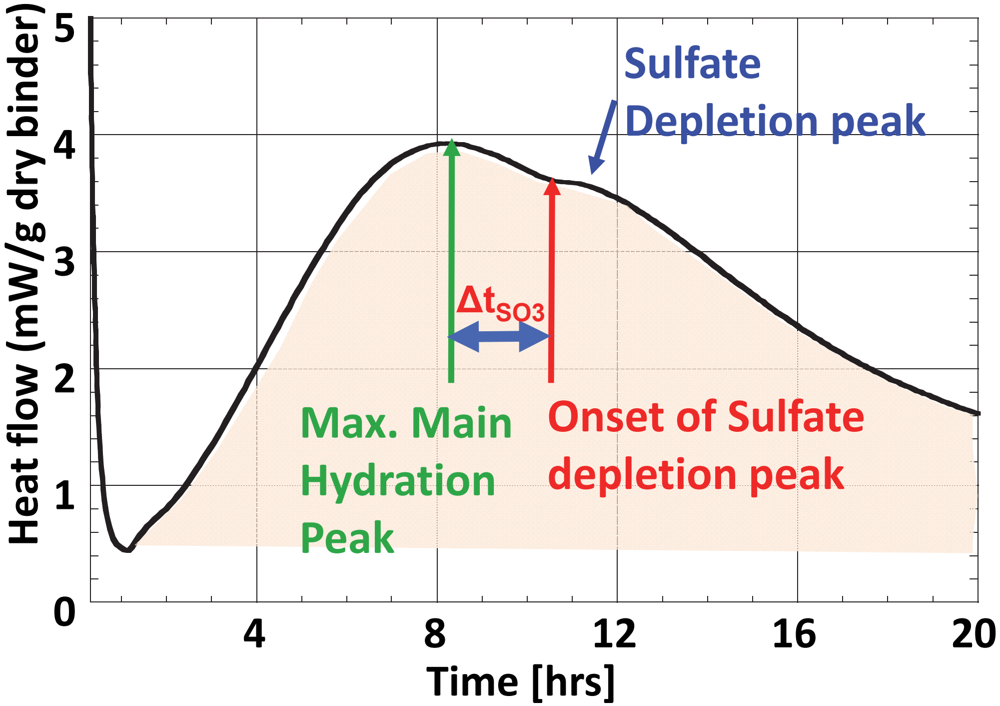
Lerch's classic work focused on straight Portland cement without admixture

Lerch used the "sulfate depletion" peak to infer when a hydrating cement is running out of sulfate in solution

At "sulfate depletion", aluminate activity increases and produces a visible "hump" by isothermal calorimetry.

Lerch postulated that enough sulfate must be present to prevent excess aluminate activity until well after the alite hydration has passed its maximum. The new ASTM C563 quantifies Δt_{SO3} for a given binder optionally tested with admixtures



Sulfate depletion peak often **NOT VISIBLE** or hard to detect for blended cements, especially with admixture

ASTM C563 therefore uses **Heat of Hydration** to find the optimum, since HoH correlates well with compressive strength for a given binder

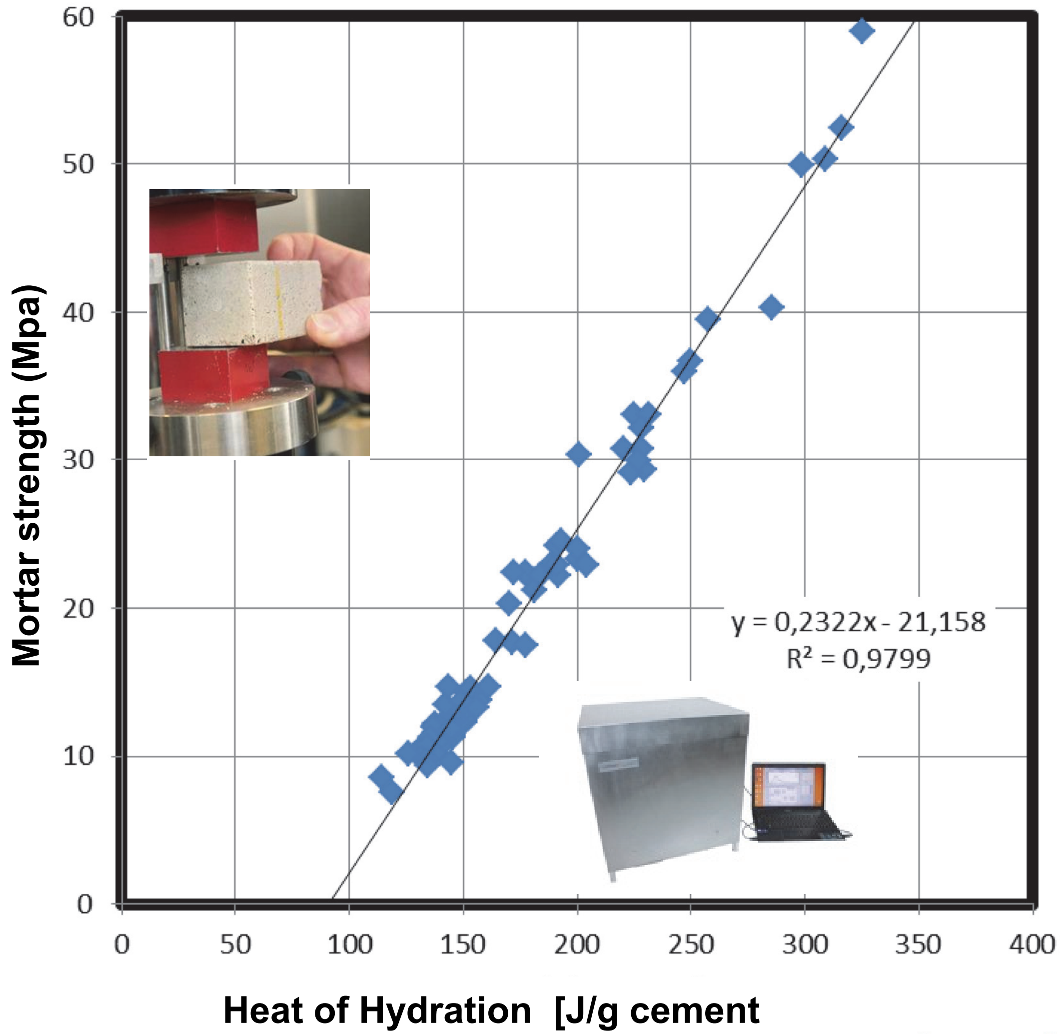
In many cases the sulfate depletion peak only becomes visible for mixes close to optimum SO3

Once Δt_{SO3} is defined for optimum SO3 using HoH, Δt_{SO3} can be used as a process control target for sulfate additions to the mill

Heat of Hydration correlates very well with strength for a given cement

Example: 1-7 day strength – Heat of Hydration (HoH) relationship in random mill grab samples of a given cement taken over a 2-yr period

- 87 Samples
- Curing ages: 1 – 7 days
- Coefficient of Variability 4 % for compressive strength vs as low as 1% for Heat of Hydration



Using isothermal calorimetry to predict one day mortar strengths
L Frølich. L. Wadsö. P. Sandberg.

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SO3 optimization by calorimetry using two industrial cement samples with a "low" and a "high" SO3: Preferred method, sulfate properly interground

Low SO3 cement
Known to be below optimum

High SO3 cement
Known to be above optimum

Prepare a series of sub samples with varying SO_3 contents ranging from low to high SO_3
Test at least 5 and preferably 8 different sulfate levels

100% Low SO3
0% High SO3

85.7% Low SO3
14.3% High SO3

14.3% Low SO3
85.7% High SO3

0% Low SO3
100% High SO3

ASTM C1702 Heat of Hydration using Isothermal Calorimetry

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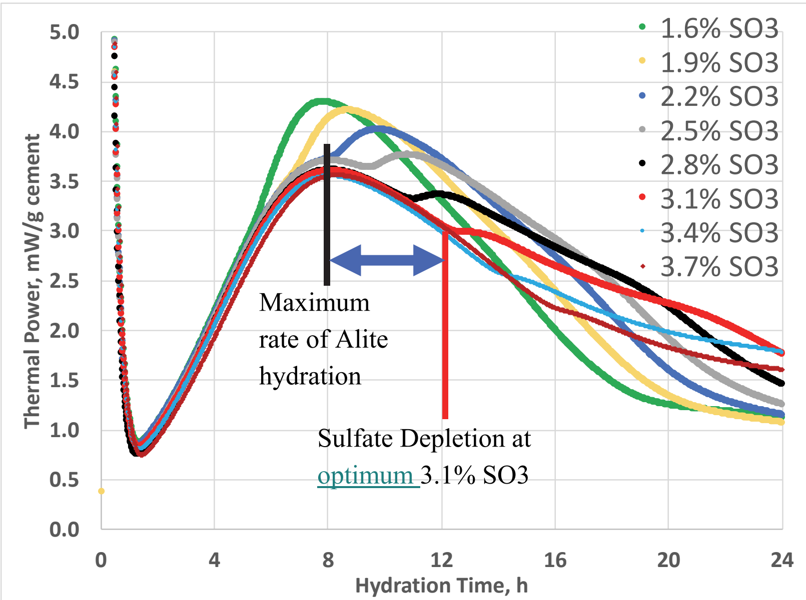
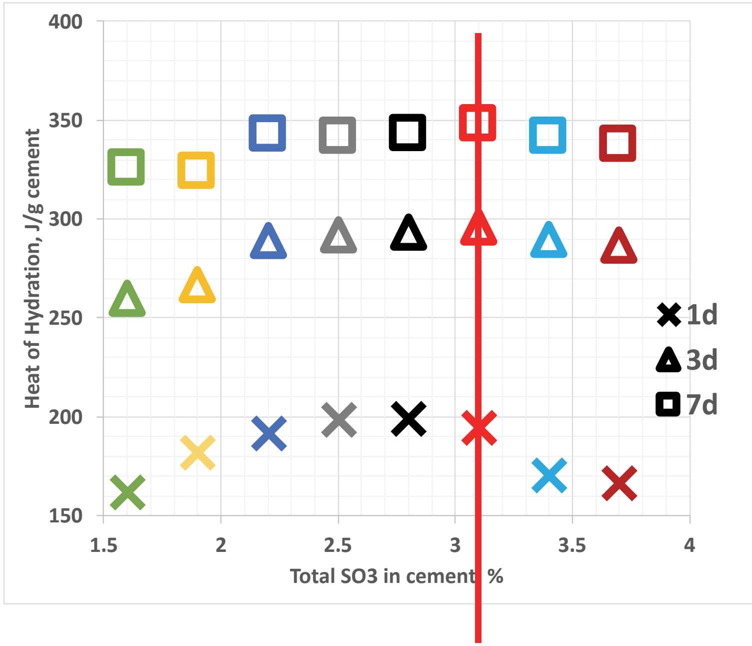
ASTM C563-18 sulfate optimization using isothermal calorimetry

- Two industrially produced cement, targeting SO3 below and above optimum
- Blend low SO3 and high SO3 cements to >5 sub samples at at range of SO3 from low to high, >2% SO3 difference from low to high
- Test for heat of hydration for 7 days, evaluate at ages of interest (typically 1d, 3d, 7d depending on cement type)
- Example shows target optimum at 3.1% SO3. Record target optimum SO3 and time elapsed from maximum rate of alite hydration to onset of sulfate depletion at optimum SO3





Target 3.1% SO3 based on HoH at 1, 3, 7d

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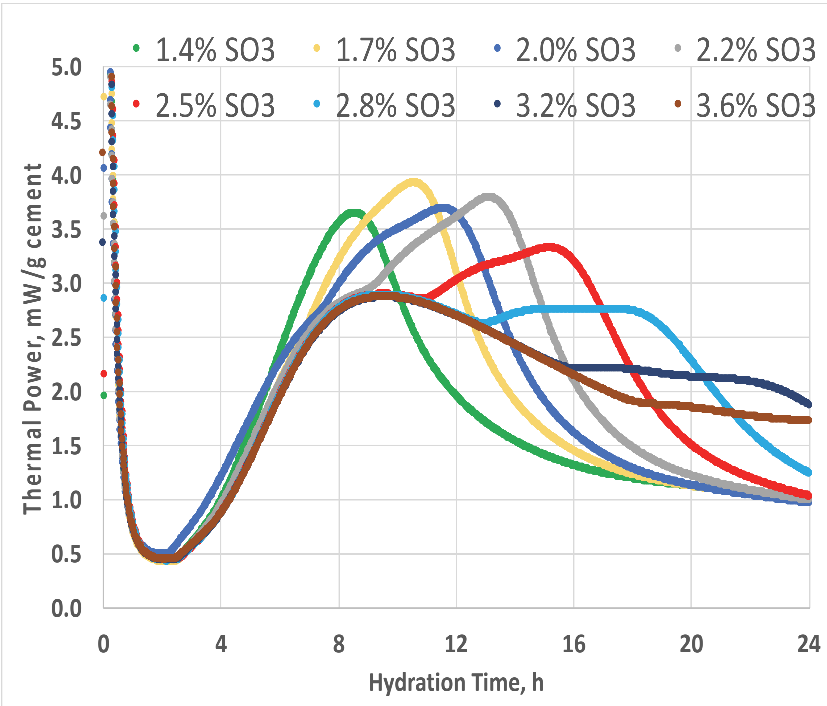
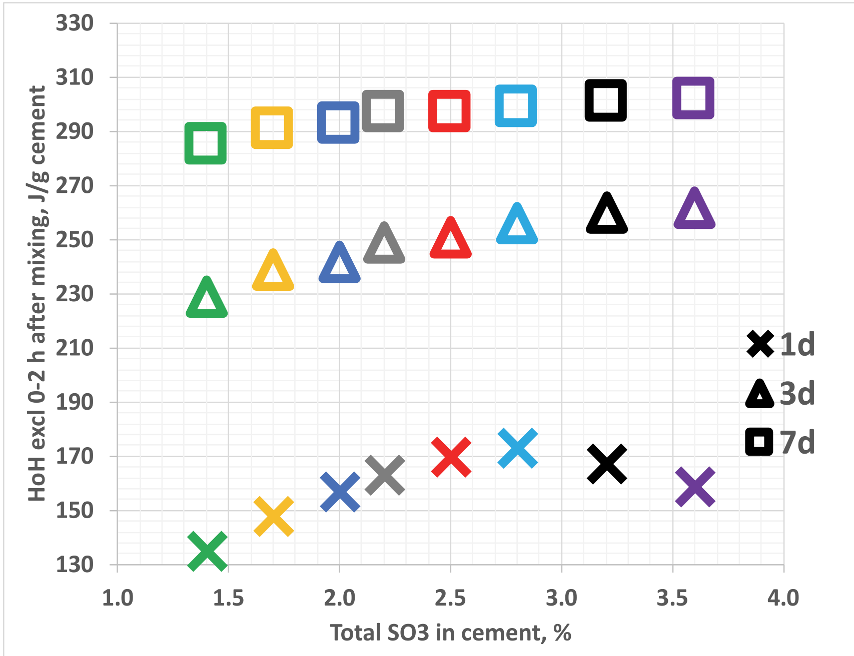
Does ASTM C563-18 "blend method" work for a European cement?

- Two industrially produced cement, with SO3 below and at optimum
- Method "A" Blend low SO3 and high SO3 cements to 8 sub samples at at range of SO3 from low to high, using careful blending in a traditional external laboratory blender
- Method "B" Weigh low SO3 and high SO3 cements directly into calorimetry sample cup and hand mix with conditioned water as in ASTM C1702
- Test for heat of hydration for 7 days, evaluate at ages of interest (typically 1d, 3d, 7d depending on cement type)
- **Results Method "A" careful pre-blending**





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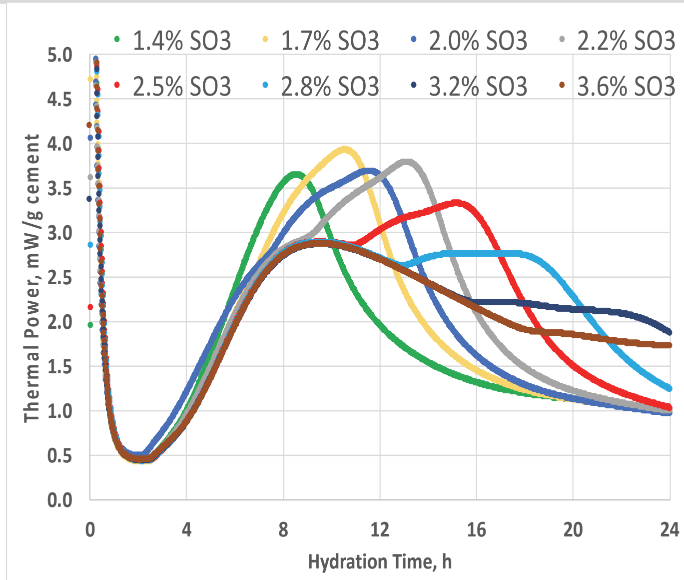
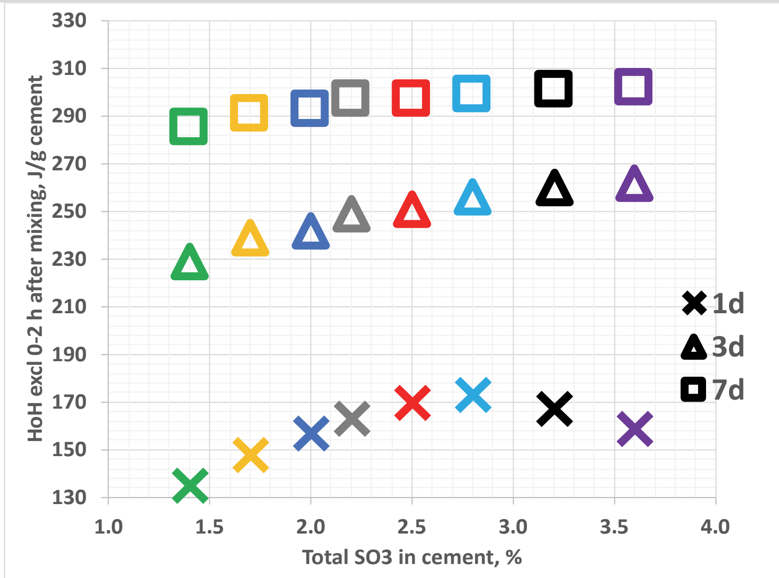
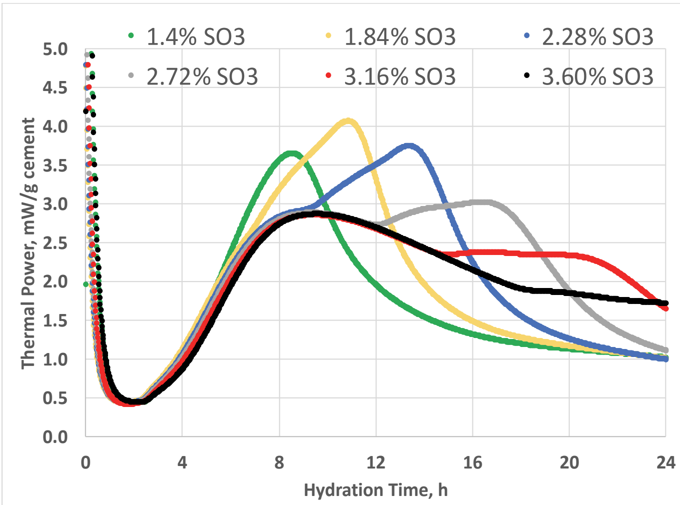
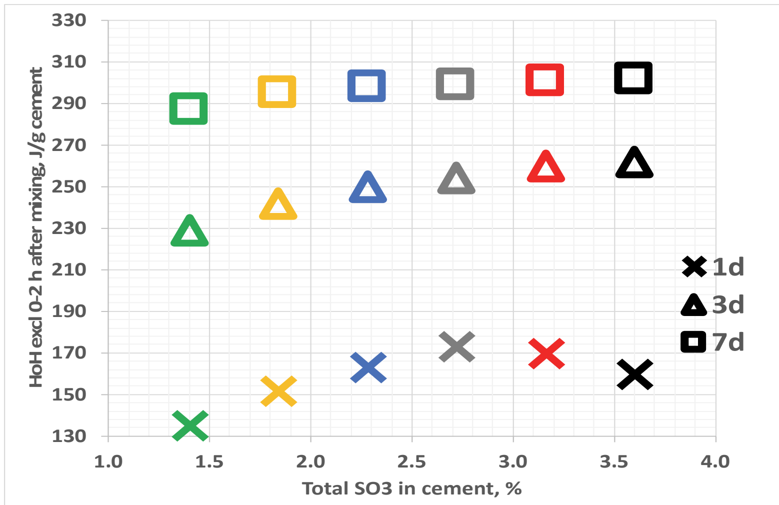
Does ASTM C563-18 “blend method” work for a European cement?





Results Method “A” careful pre-blending





Results Method “B” weigh low and high SO3 cements directly into calorimetry sample cup without pre-lending

SO3 optimization by calorimetry using one industrial cement samples with a “low” SO3: “Addition” method, study effect of sulfate forms, etc

Low SO3 cement

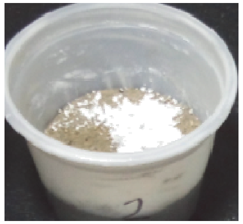
Known to be below optimum

Calcium sulfate

Laboratory or industrial

Add calcium sulfate to cement to obtain a series of sub samples with varying SO_3 contents ranging from low to high SO_3 .Test at least 5 different sulfate levels

No sulfate addition



Lowest sulfate addition

Second highest and highest Sulfate addition

ASTM C1702 Heat of Hydration using Isothermal Calorimetry

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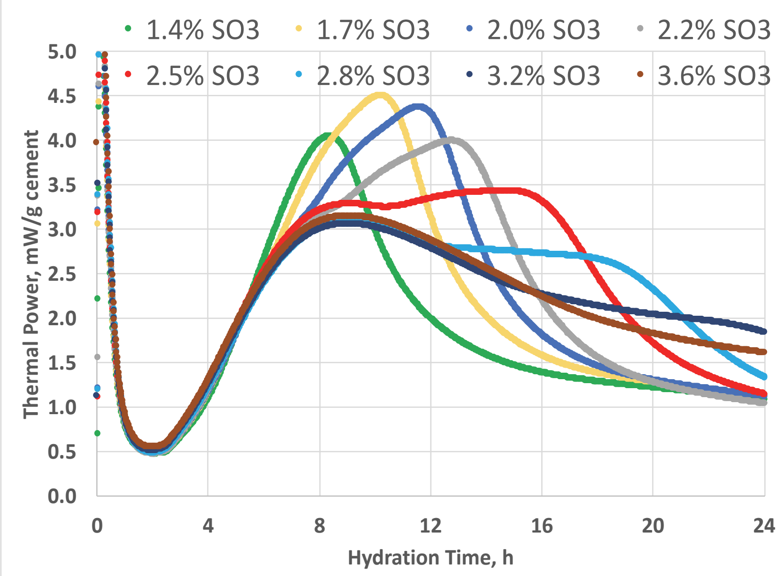
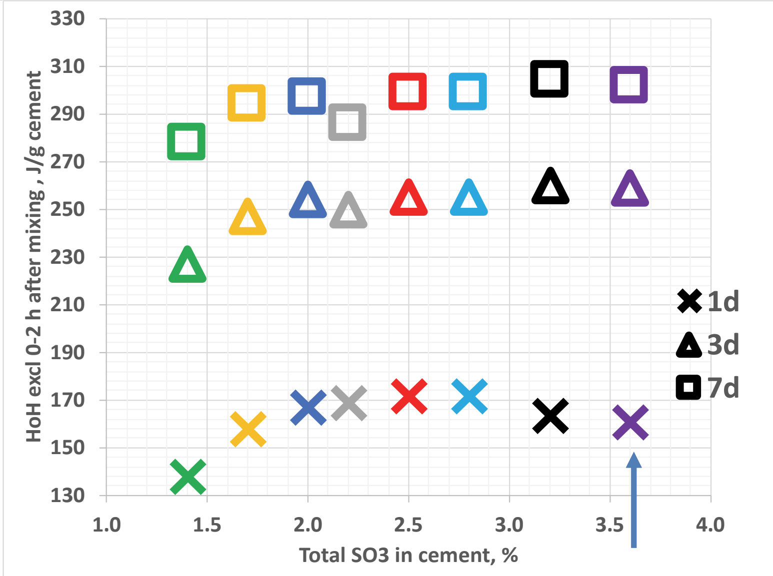
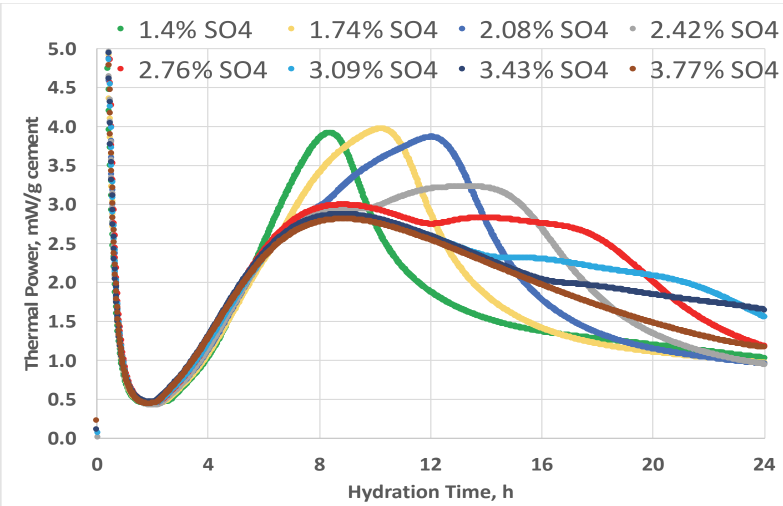
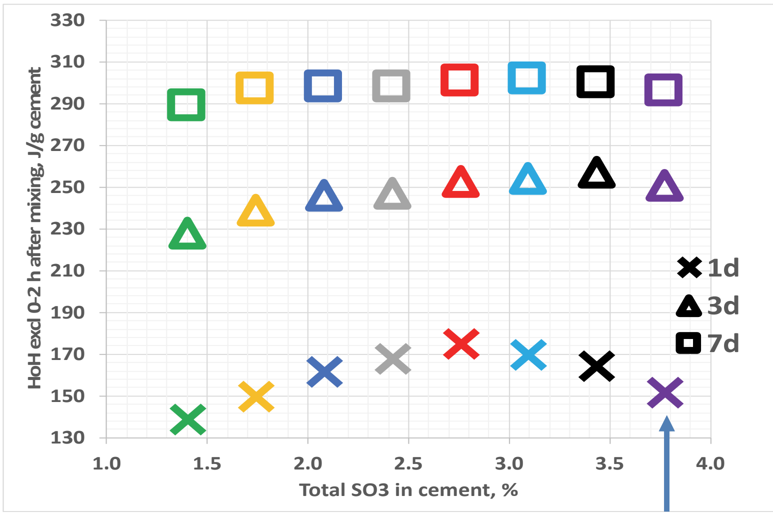
Does ASTM C563-18 “addition” method work for a European cement?





Results Method “A” careful pre-blending sulfate addition in cement





Results Method “B” weigh low SO3 cement and sulfate additions directly into calorimetry sample cup without pre-lending

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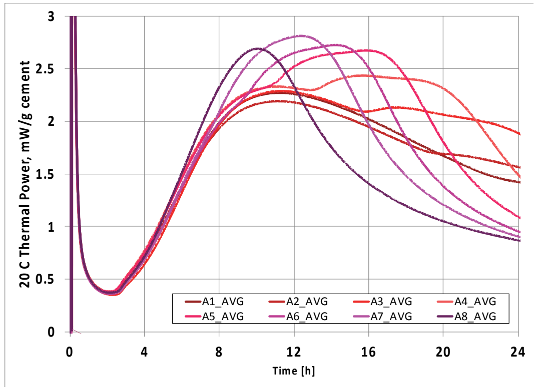
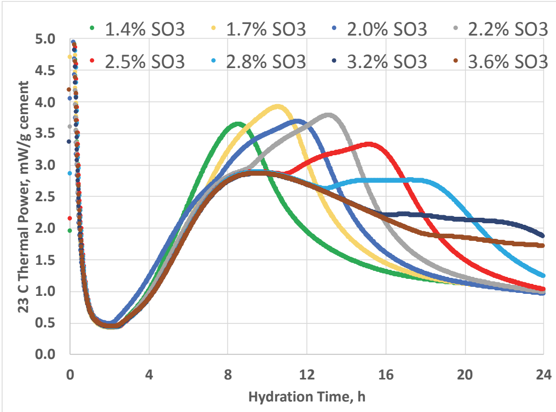
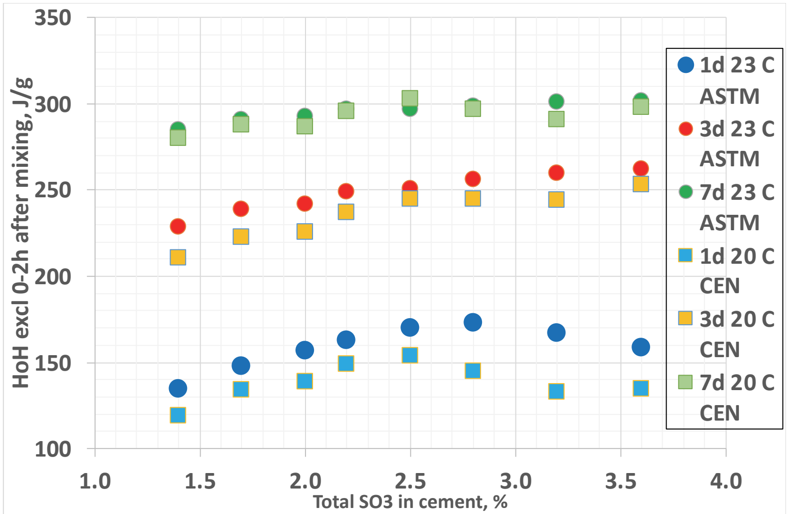
How does CEN testing at 20 C compare vs ASTM testing at 23 C

20 C CEN



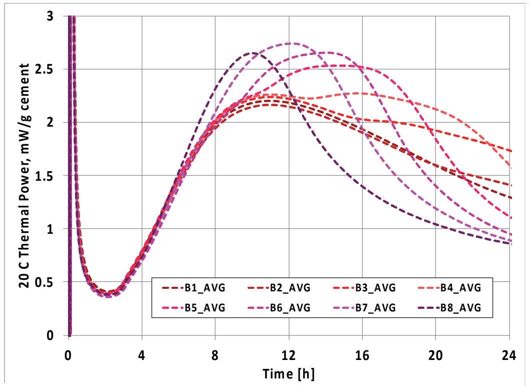
23 C ASTM



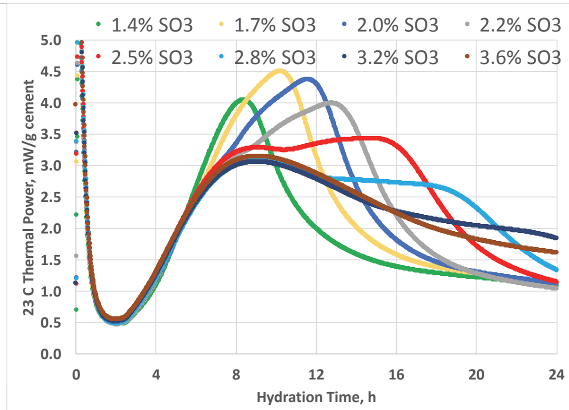


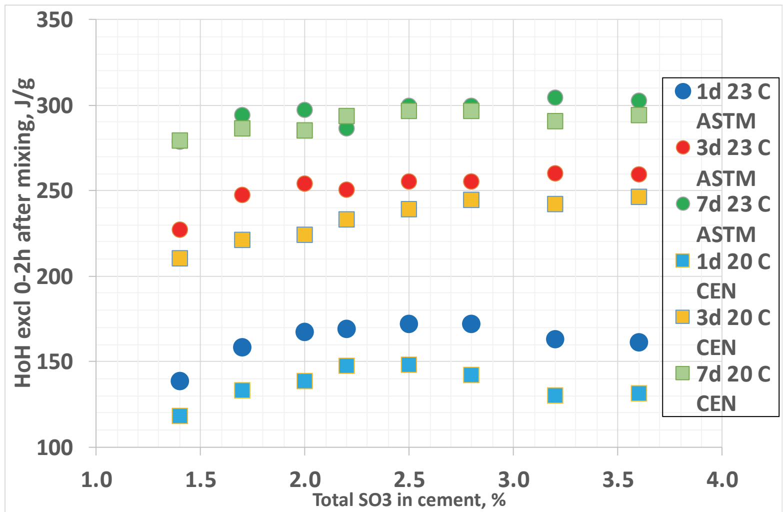
Results blending low and high SO3 cement

20 C CEN



23 C ASTM





Results adding calcium sulfate to low SO3 cement

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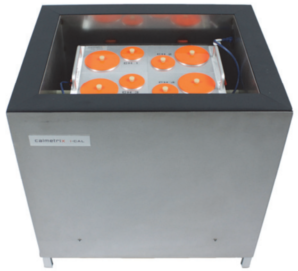
Calorimetry is a lot easier than strength testing

- Labor intensive (and messy)
- Inconvenient – operator has to be there to break cubes at right curing time
- High variability, especially if tested with admixture
- Requires curing chamber



- Takes only minutes of sample prep
- Nobody needs to be there at curing time. Load samples, walk away for the weekend
- Very low variability
- The calorimeter is the lab / curing chamber

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Test for HoH according to ASTM C1702 or the new European soon-to-come standard for desired test age, minimum 24 h and preferably 7 days

ASTM C563 optional test parameters

- Include supplementary cementitious materials (SCM) beyond blended cements
- Include admixtures
- Test of effect of non standard temperature

- Test temperature, addition of SCM and admixtures are all known to impact the optimum SO3.
- **Be mindful of the effect of mixing energy when testing for the effect of dispersing admixtures and retarders**
- The optimum SO3 typically increases with the test age and with use of admixture

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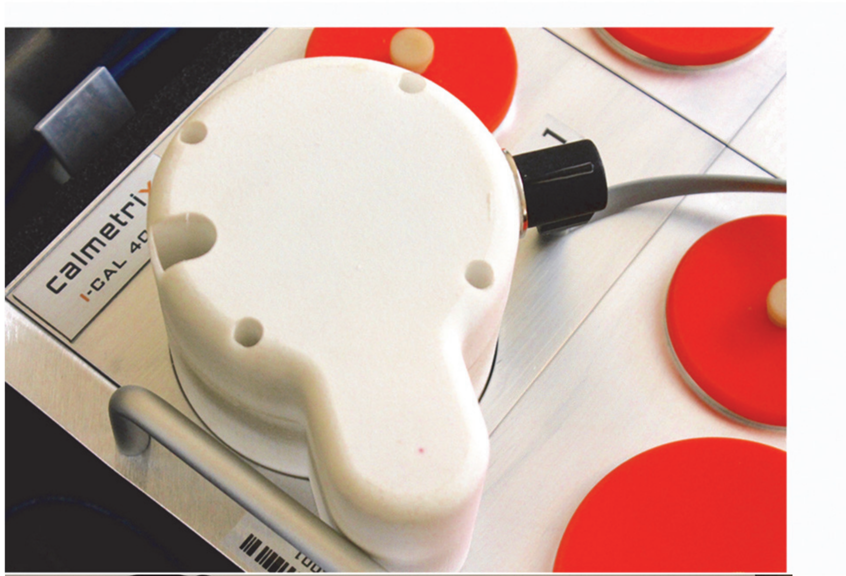
Calorimetry is a lot easier than compressive strength testing, but it still takes some operator time:

- It takes 2 hours for the water to stabilize at the isothermal temperature
- Operator has to prepare the sample in two steps
- One might be worried about the variability of mixing manually

Calmetrix developed a true internal mixer for cement mortar (or paste):

- Mortar important for relevant mixing energy with admixture
- Cement sample and water are loaded into different containers
- Mixer and measurement start automatically once materials are at a stable temperature
- Users can define mixing speed / angular steps / torque / duration
- Easy to automate
- Also suitable for dry mortar testing



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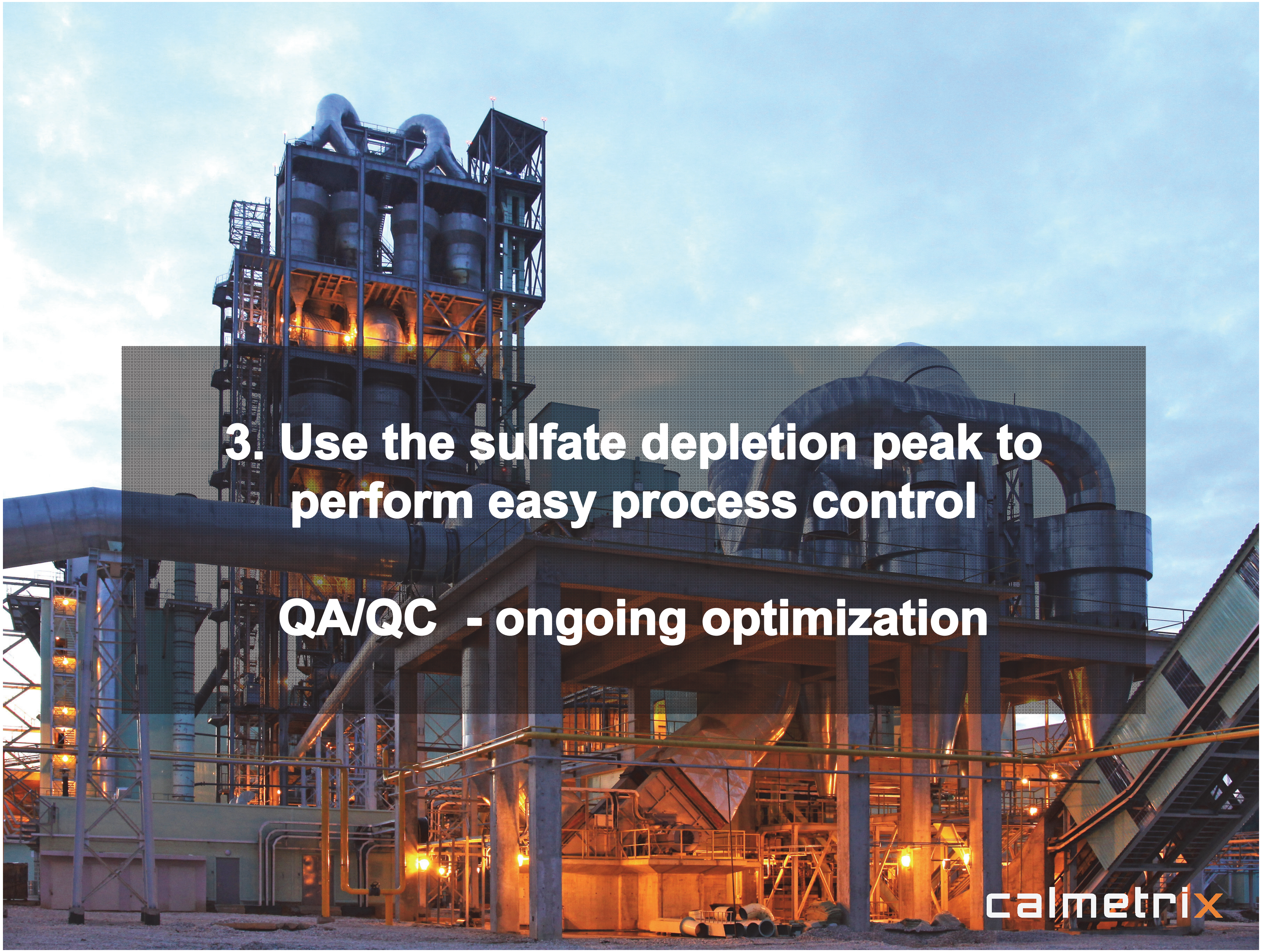
3. Use the sulfate depletion peak to perform easy process control
QA/QC - ongoing optimization
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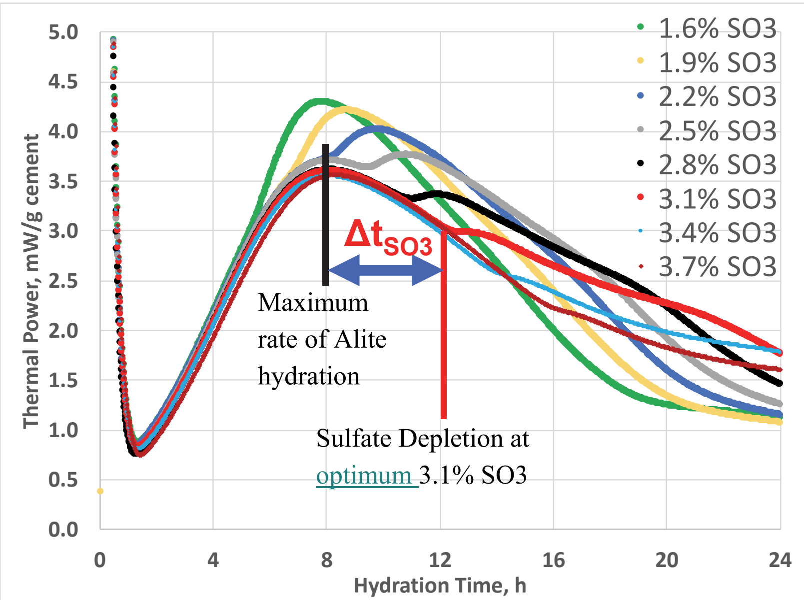
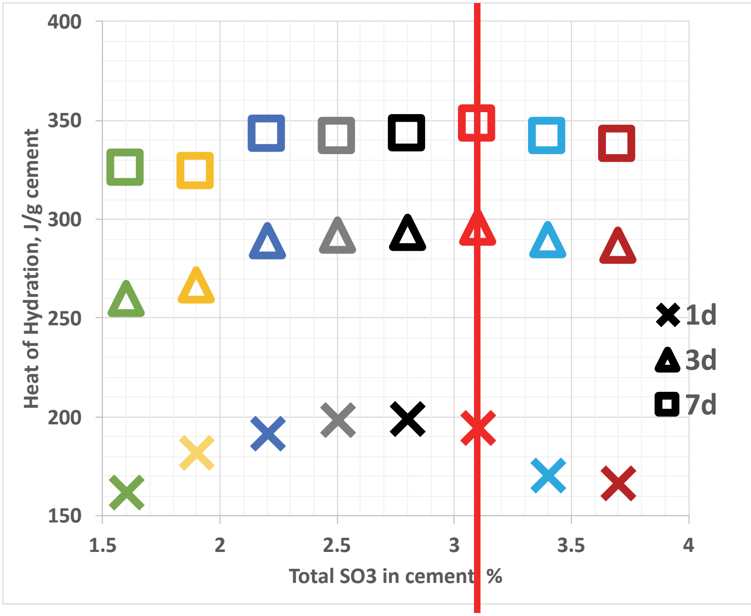
Process control procedure for sulfate addition to cement mill

After completed optimization using Heat of hydration (paste without admix or mortar with admix), define Δt_{SO3} as the time lapsed between the maximum of the main peak and the onset of the sulfate depletion peak at optimum SO3

Producers often deviate from "paste optimum SO3" based on early stiffening issues, or concrete admixture demand. Accordingly, Δt_{SO3} is adjusted higher or lower based on other performance tests.





Target 3.1% SO3 based on HoH at 1, 3, 7d

Process control procedure:

- Each time a mill sample is taken, run a calorimeter test
- Determine the Δt_{SO3} for the sample and compare to the Target Δt_{SO3} from optimization tests (including adjusted Δt_{SO3} based on concrete etc if needed)
- If $\Delta t_{SO3} \neq$ Target Δt_{SO3}, adjust sulfate addition to mill to get back to Target
- The whole procedure only takes a calorimetry test. The software does the rest

QUESTIONS ?

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