Limestone Particle Size and Cement Performance: Can we apply Calorimetry for Process Control ?

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4th European Cement Calorimetry Conference
Dresden 11-13 December 2018

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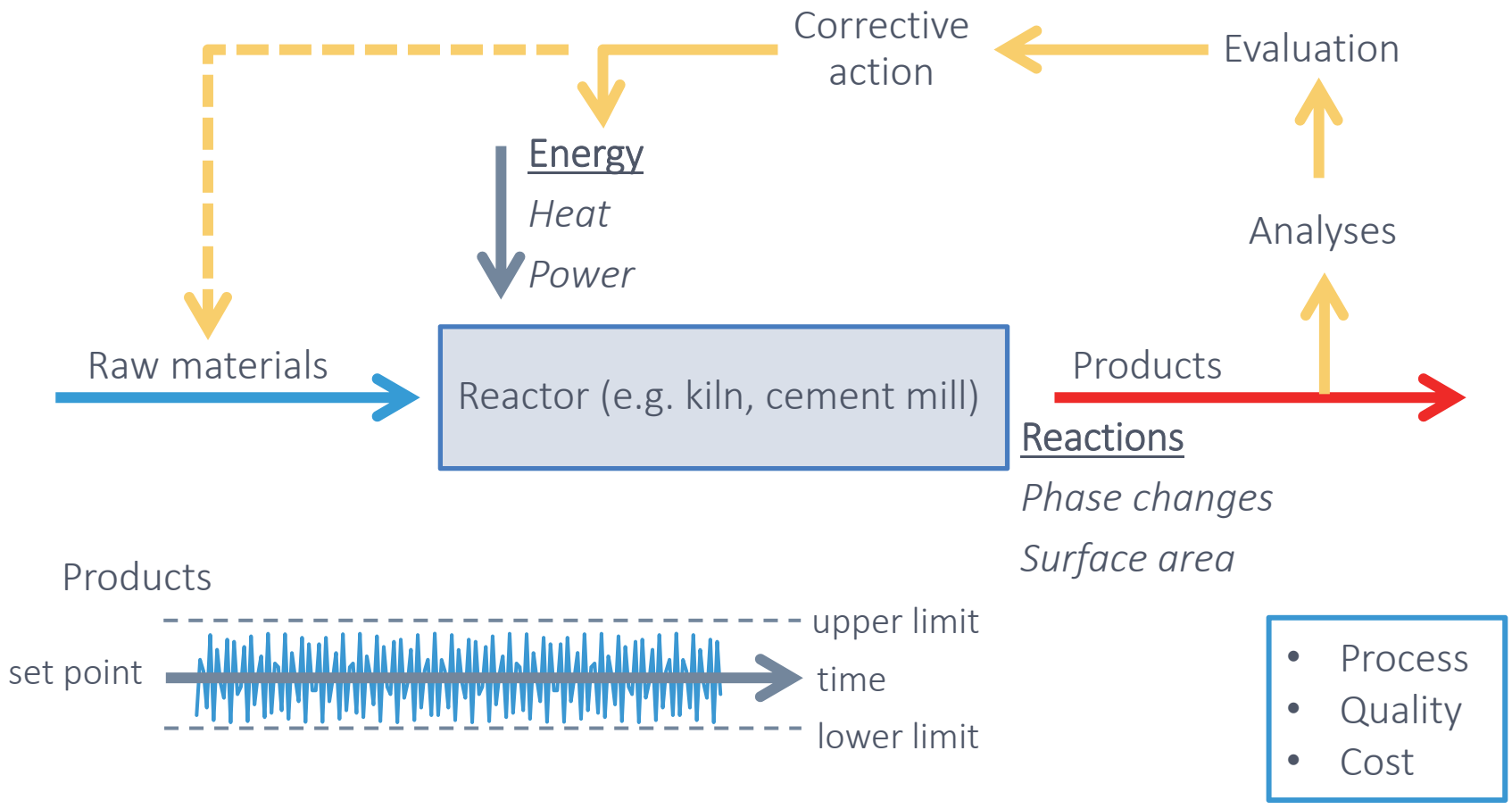
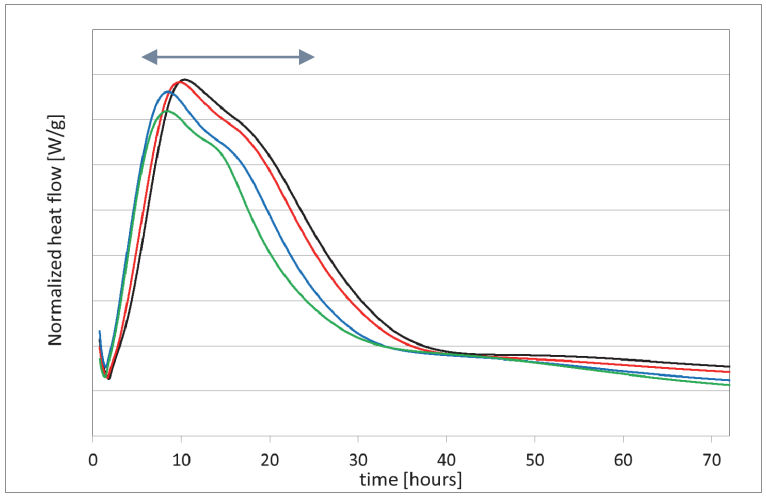
Process control

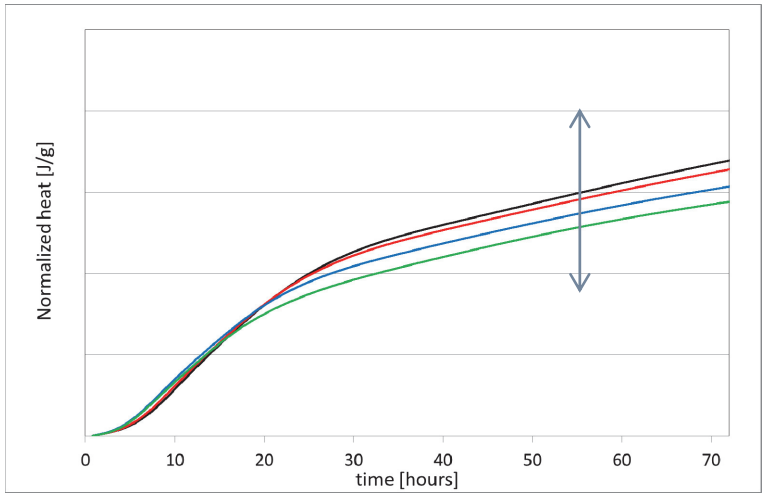


What happens in calorimetry if you change just one component in cement ?



Fundamental parameters driving signal

- Particle size
- Reactivity of various constituents
- Sulfate carrier

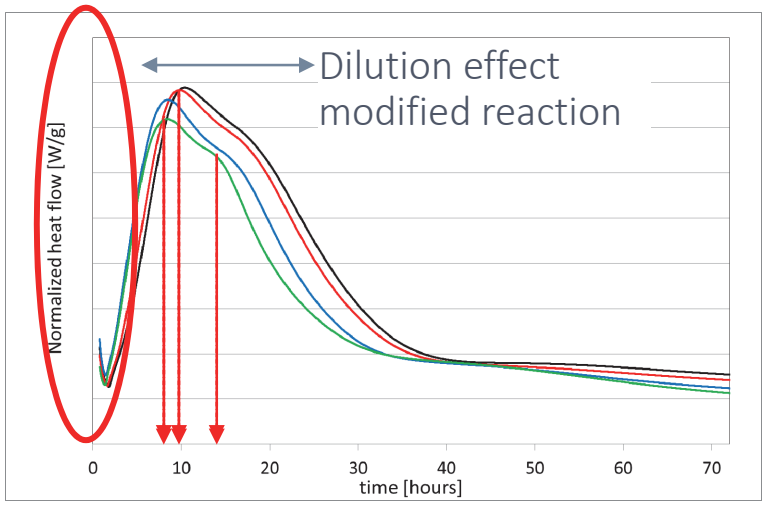


Sample handling

- Sample preparation: often manual
- Admixtures
- Temperature: modify kinetics

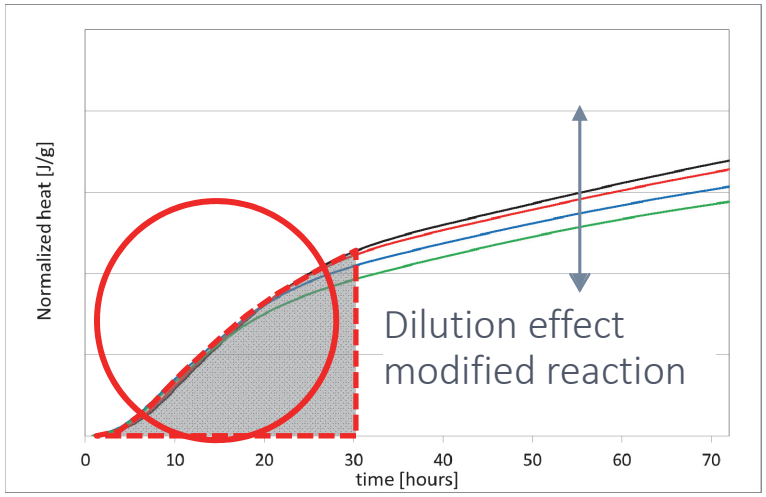
Often it’s a verify descriptive usage of the calorimetric pattern

Calorimetry. What can be extracted from a cumulative signal ?



A time max. rate at

- Main peak
- Sulfate peak
- …

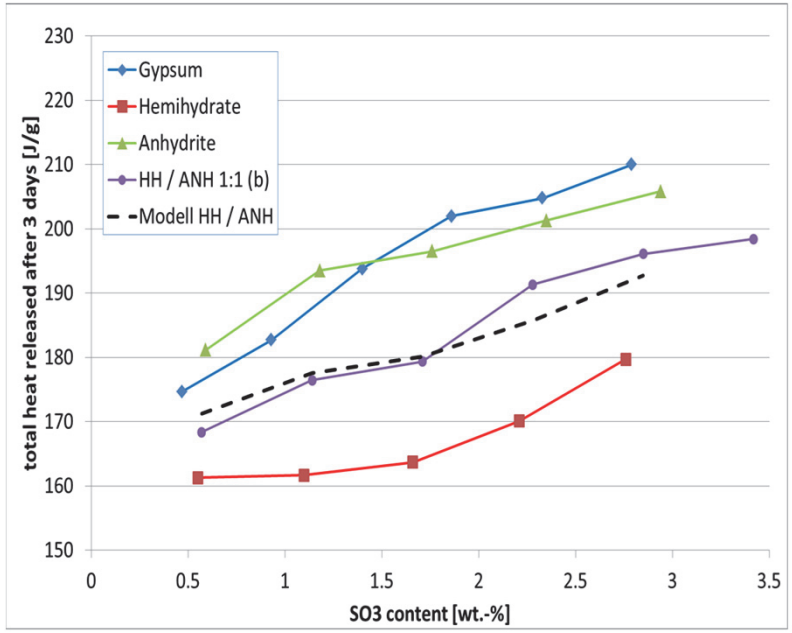


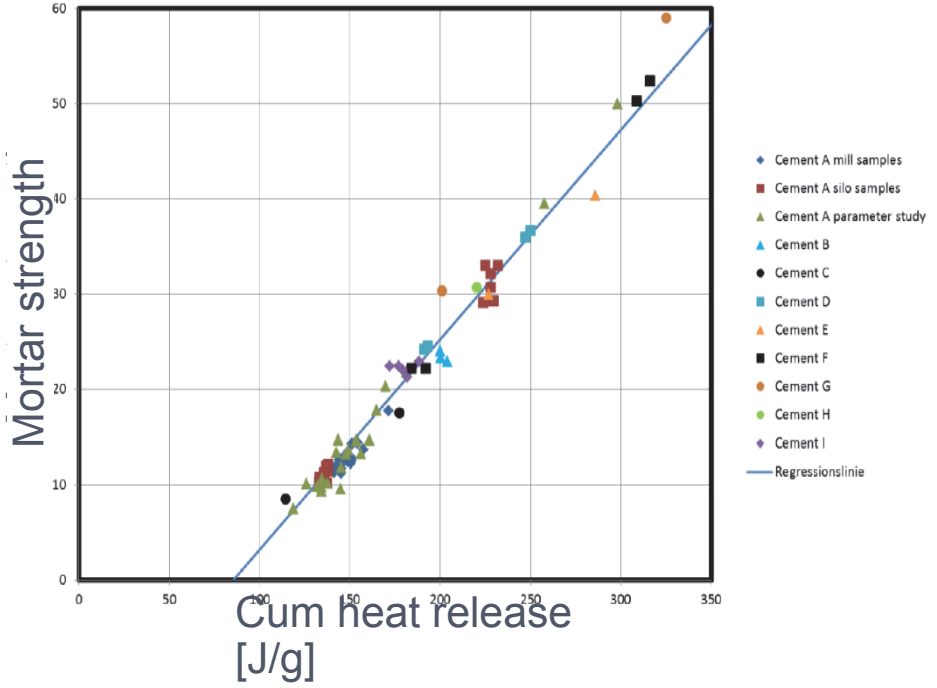
An energy release value

- at X hours
- A ratio at x hours / y hours
- A difference ….

- Missing first peak in standard measurements / dynamic slope
- Speed is critical for process control: dispatch is close

Is there potential ? Examples





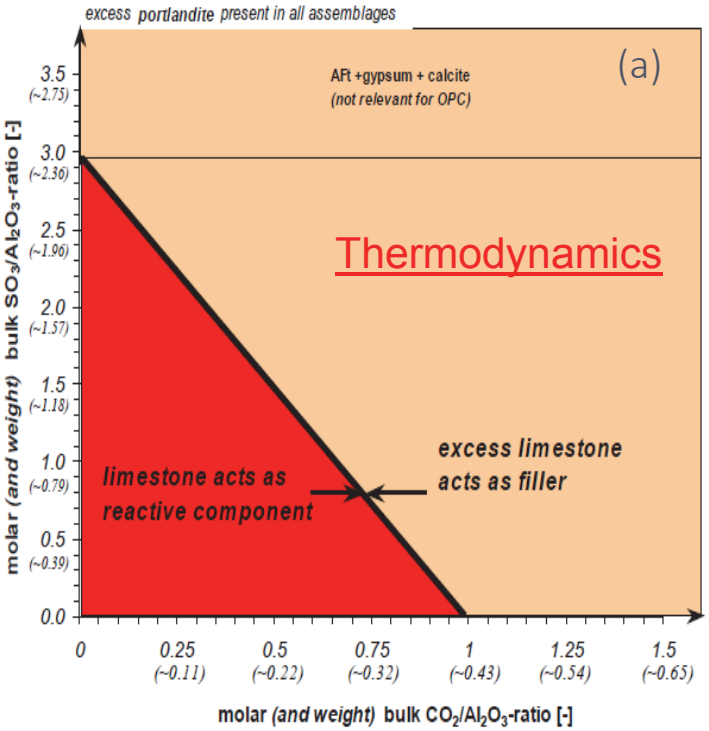
- Total heat release related to sulfate carrier
- HoH correlates with strength

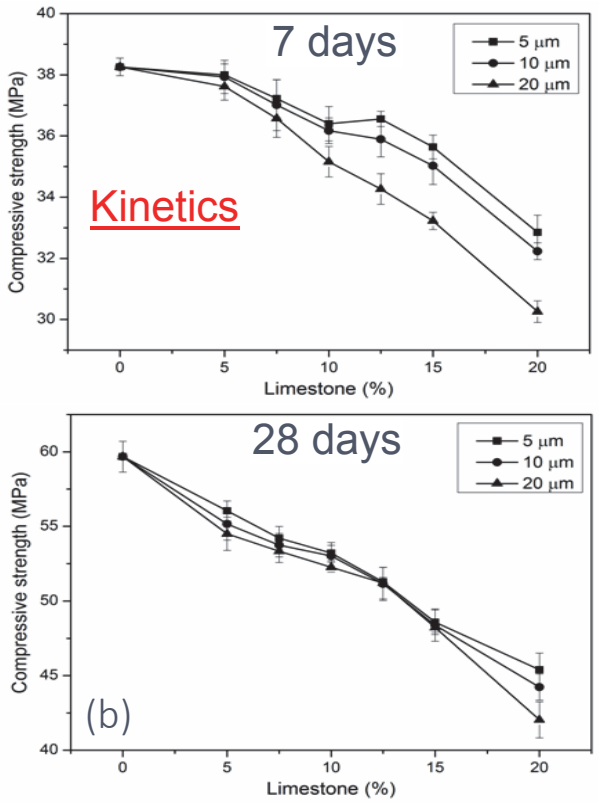
Source: tkIS data; Froelig, Engstig: Calorimetry workshop Berlin 2014

Could physical testing be partially replaced by calorimetry ?

	Mortar data	Calorimetry
OPEX/CAPEX	• Sand/Mixer+Moulds+Basins/Strength tester	• Ampoules/*Mixer*/Calorimeter
Sample preparation	• Simple/Employees/ Human error	• Simple/less Employees/Human error
Automation	• Difficult: depends on local norm	• Possible
Time requirement	• Weeks (up to 28d or longer) • 24h composite: three spl/week (EN) • No acceleration option: regulated	• ≤ 7 days • Frequency depends on available cells • Speed option at increased temperature
Continuity/Sample history	• Discontinuous/destructive	• Continuous/non destructive, but paste..
Data evaluation	• Simple	• Educated personnel required
Additional information	• Set (Penetrometer) • Water demand/Workability	• To be developed • What can be read from curves
Accuracy	• Long dates OK, short dates critical	• Accurate and reproducible; Which data is indication for phys. testing ?
Relevance	• Cement industry has to do (Norm) • Little transfer from mortar to concrete	• Limited regulation (e.g LH cements) • "Secondary standard"
	Mortar is standard	At lot of work to do

Why we picked PLC….

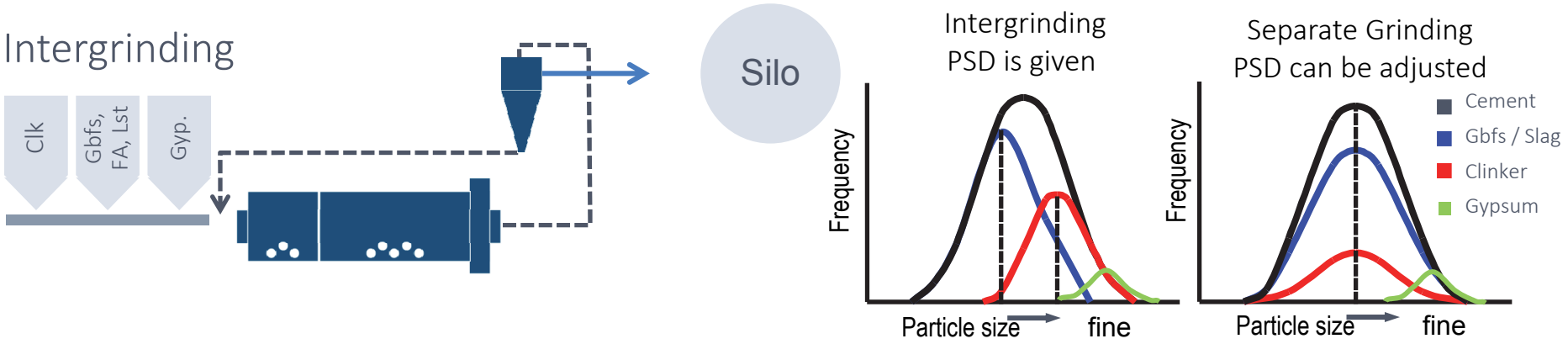




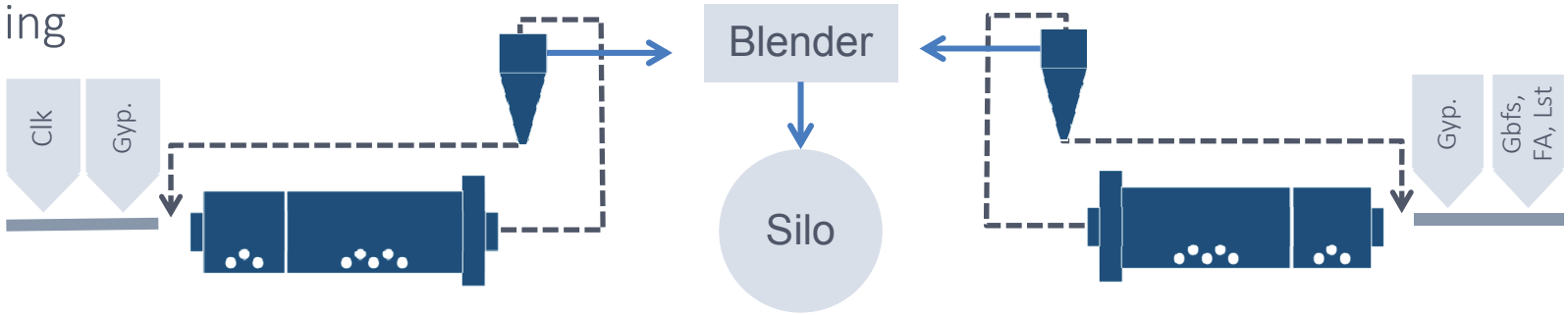
* Images sources (a) Th. Matschei (2006): (b) P. Thongsanitgarn, W. Wongke, S. Sinthupinyo, A. Chaipanich (2011),

Why we picked composite cement ….

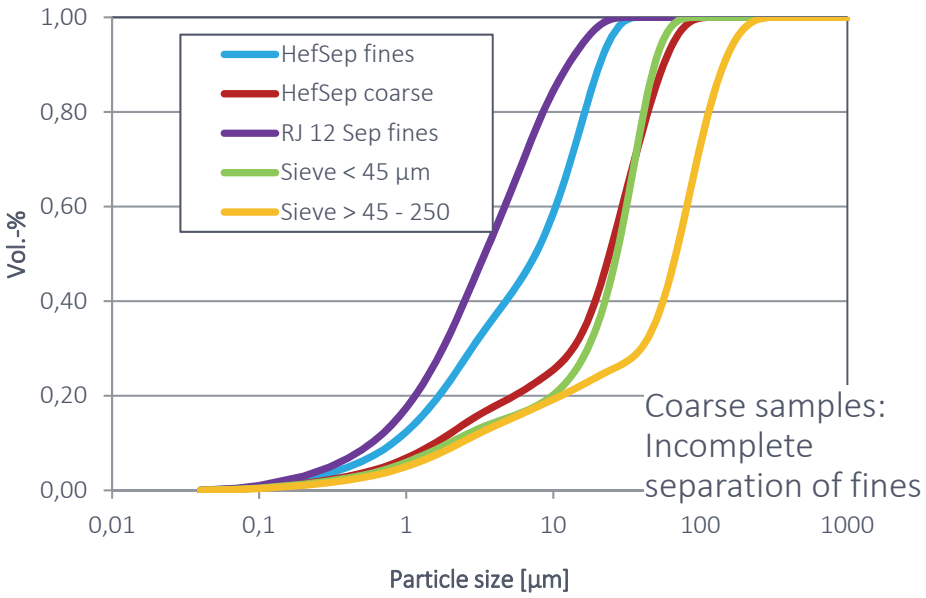
Intergrinding



Separate grinding

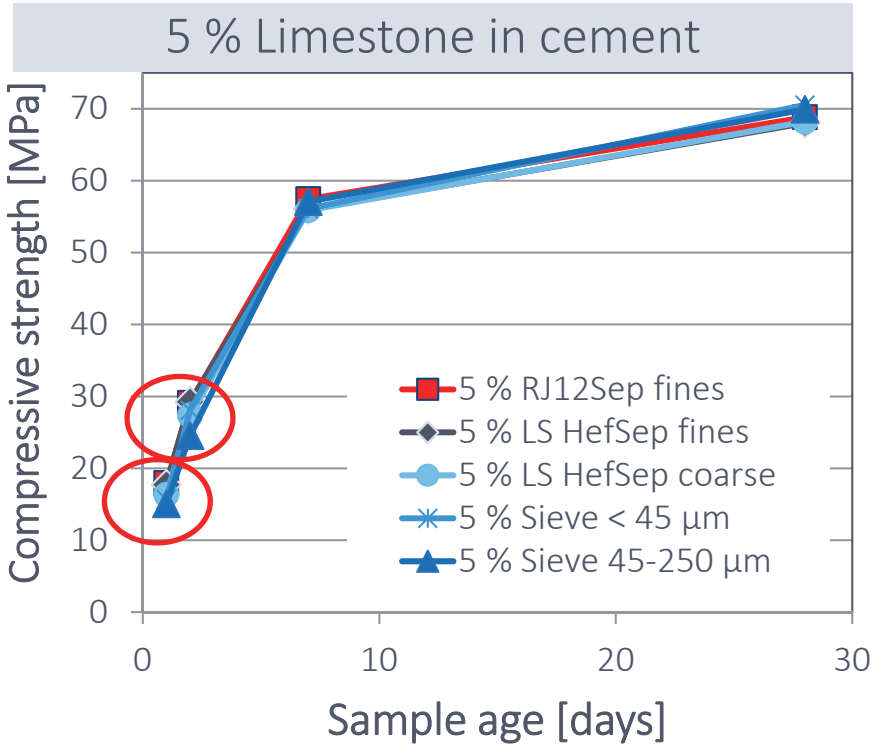


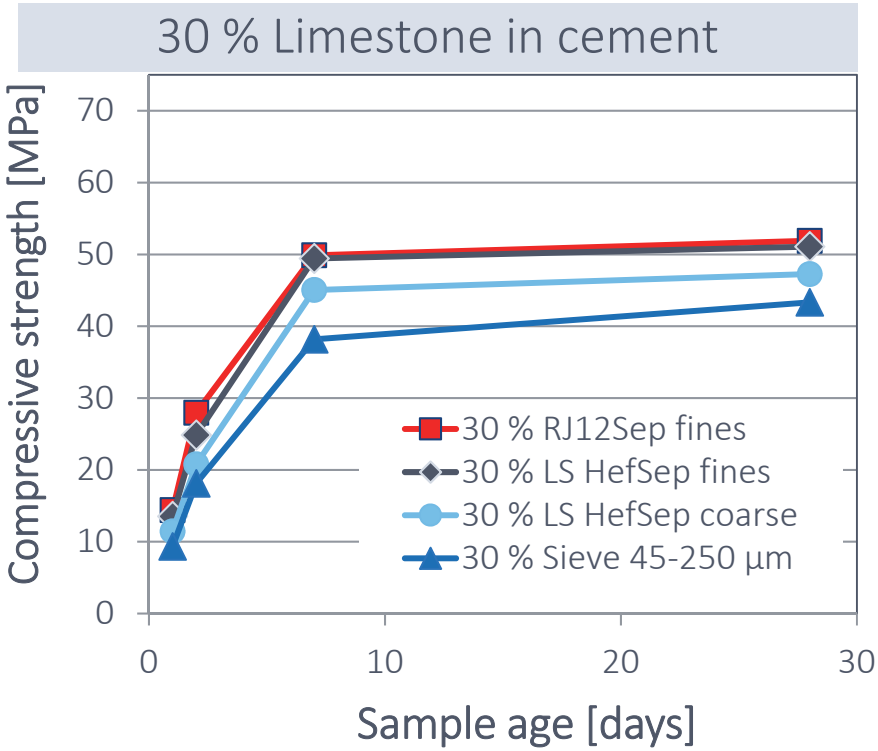
Materials and testing

Standard Cement	Limestone
• Clinker from same source (C3S 73.2 wt.%, C2S 7 wt.-% ,C3A 5.5 wt.-%, C4AF 12 wt.-%)	
• Sulfate carrier as industrial cement (4.7 wt.-% at HH 50% Anh 50 %, commercial source)	
• Cement production on a pilot plant scale VRM at 4000 Blaine • Pilot plant cement: 5 %, 10%, 20% and 30% of limestone size fraction	
• Cement testing: EN mortar and const. flow, calorimetry (TAM air), XRD of hydrated paste	

- Direct monitoring of limestone particle size impact(surface area, solubility …).
- Resembles conditions for separate grinding of limestone cement.

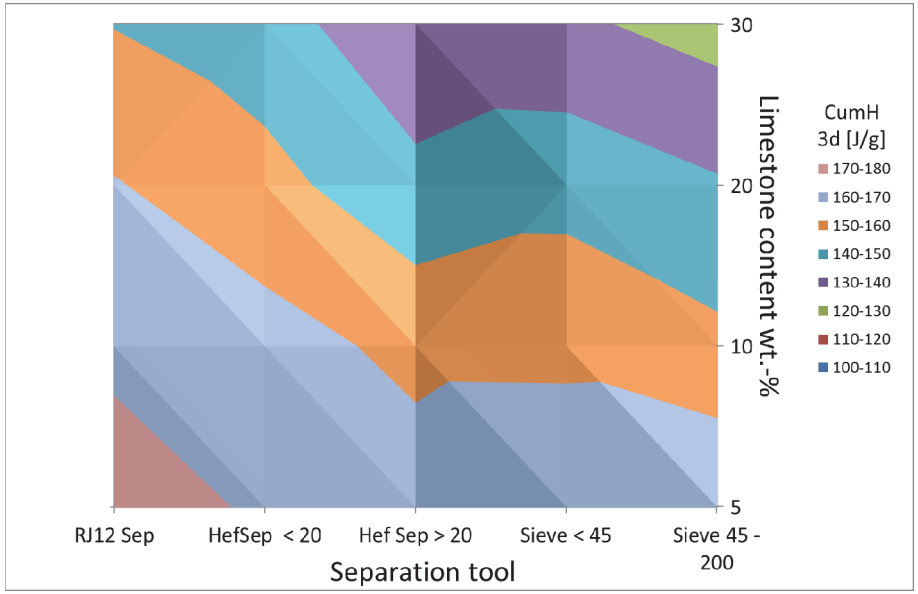
Compressive strength development





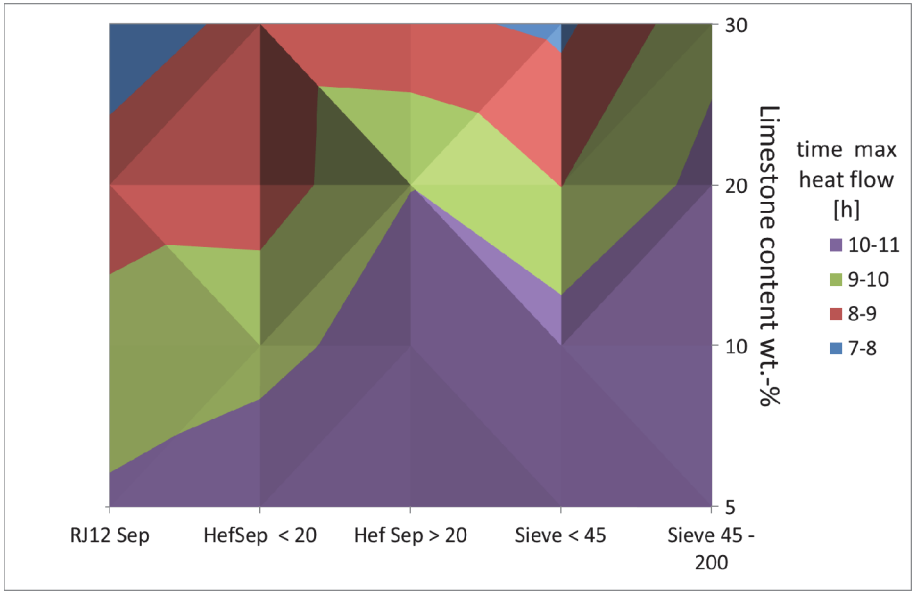
Is this information seen in calorimetry ?

Heat of hydration related to limestone content and particle size



- Fine grained limestone contributes to heat of hydration
- Still the required time would be on typical mortar testing

The first signal would be maximum heat flow…



Data assessment

- Collection of data from calorimetric curve difficult – tips on top of peak possible
- Attribution of “intensity” to reaction
- “Secondary standard” approach calibrate the system

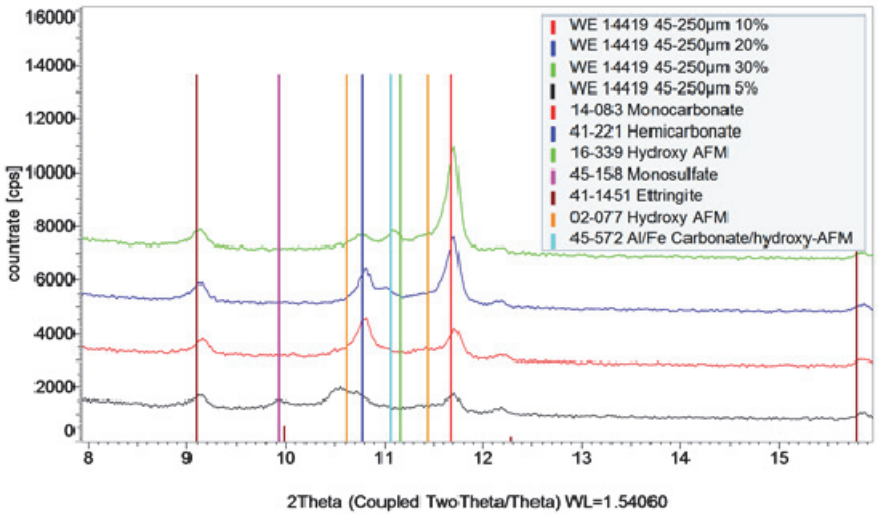
Learnings

- Availability of CO_2 relative to SO_3
- Fine accelerates reaction. Could be a move of silicate or aluminate contribution.
- Coarse lime stone is retarding

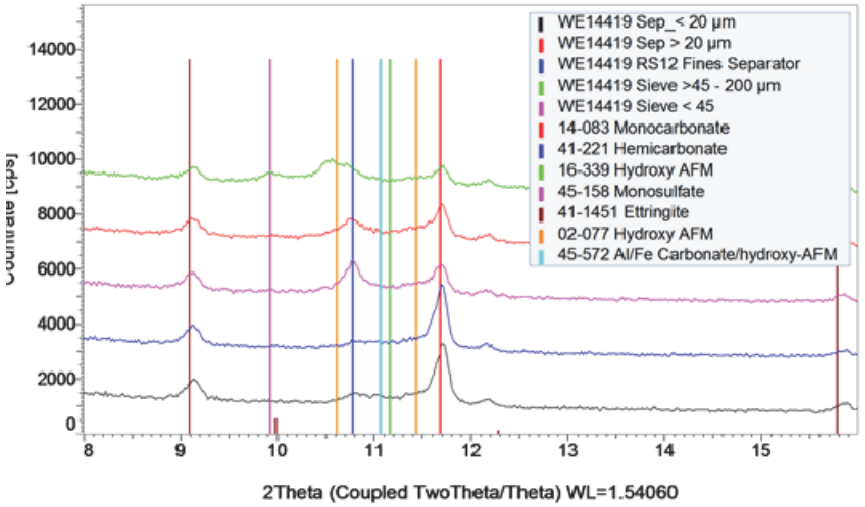
- Process relevant data after 7 – 15 hours: faster than mortar testing
- Without having final answers ….

XRD analyses on stopped hydrated samples (28d): What is behind ?

Coarse limestone 45-250µm



5 % Limestone various fineness



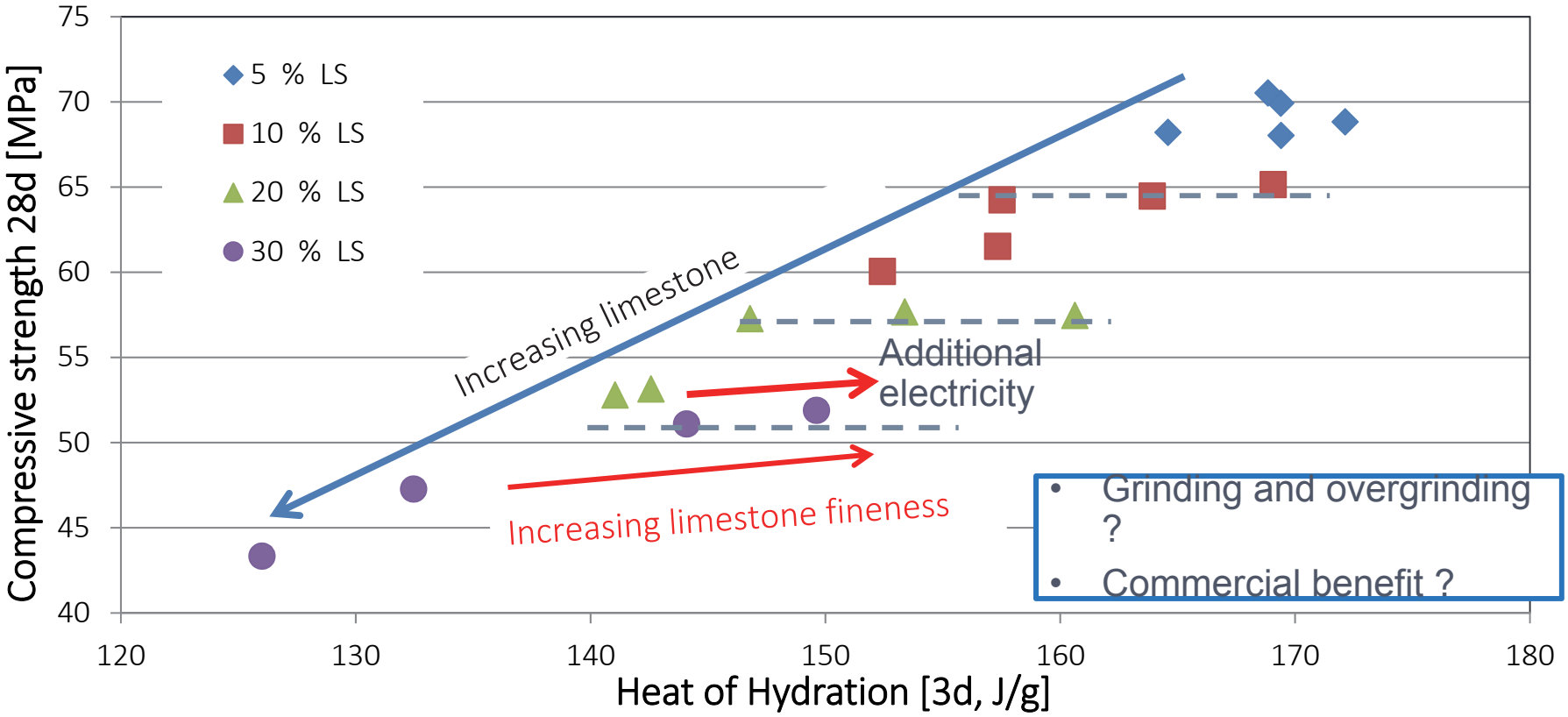
Increasing CO_2 in solution

- Hydroxy-AFM → Hemicarbonate → Monocarbonate

Fineness and concentration

Samples stopped after 28d, analysed by qual XRD

Cumulative heat after 3 d correlates to 28 compressive strength



Conclusions

- Limestone
  - Fines particles contribute to strength and heat release
  - Limestone surface area and concentration modify hydrate composition
- Calorimetry in process control
  - Still signals need to be identified
  - Calorimetric data supports strength observation
- Calorimetry could be the next step in lab automation for cement industry
  - Support kiln operation for clinker reactivity
  - Support cement grinding for process control
  - Support R&D by reducing physical test requirement

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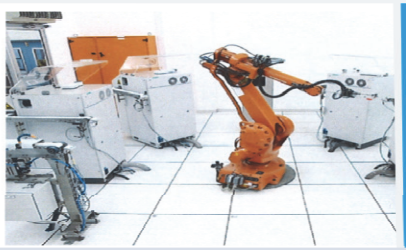
Laboratory Automation



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