Sustainability in the Cement Industry: Thermodynamic Modelling of Belite Cement Clinker

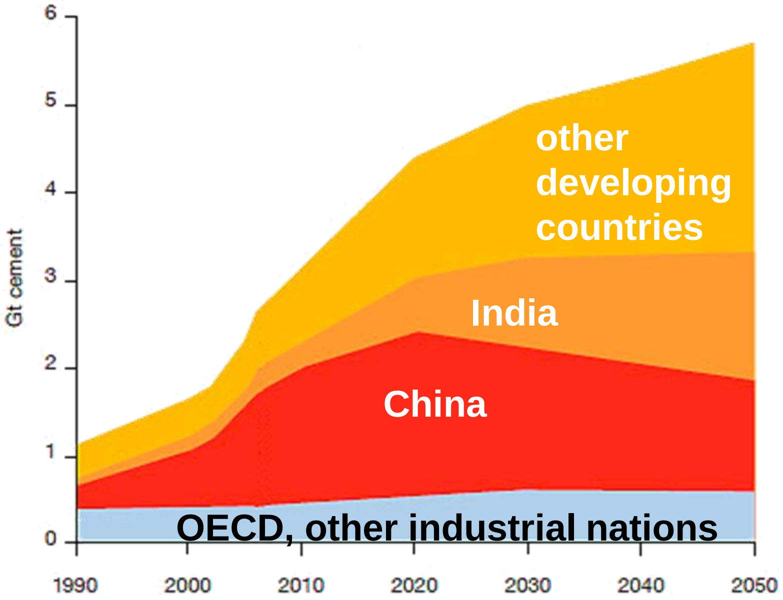
Annual meeting of the DECHEMA high-temperature technology specialist group

P. Yarka Reddy, G. Sandaka, G. Beuchle, P. Stemmermann, D. Stapf

Introduction & Motivation

Karlsruhe Institute of Technology

Forecast of cement production[1]



- Cement: responsible for 5-7% of the global CO_2 emissions[2]
- Increasing trend in cement production:
  - Increase in CO_2 emissions
  - Increase in raw material utilization
  - Energy efficiency (cement production is an energy-intensive process)
- End-of-life demolition waste becoming a significant problem

⇓

Need for circularity in the cement industry

[1] https://geopolymerhouses.wordpress.com/2011/09/18/a-blueprint-for-a-climate-friendly-cement-industry/ (15.3.2024)
[2] Robbie M. Andrew 2018 Global CO_2 emissions from cement production, 1928-2017

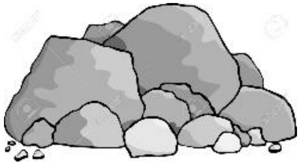
Concrete fines to feedstock route: ITC Belite process

Crushed concrete
Fine particles

+ $CaCO_3$

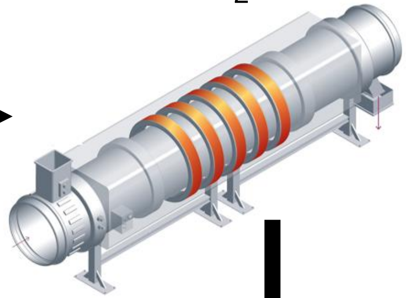
Typical fines composition
CaO/SiO_2 molar ratio = 0.68

Demolition



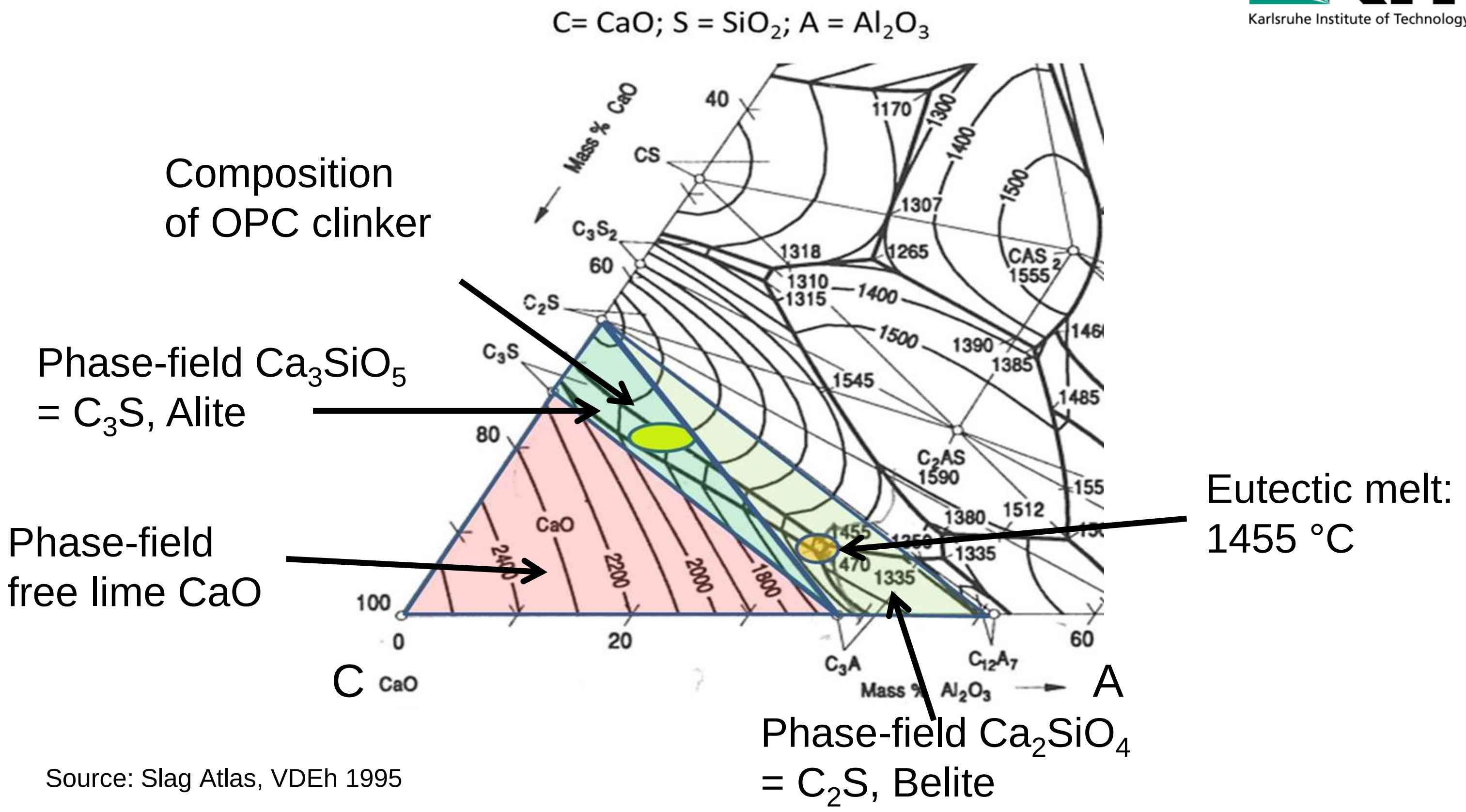
Crushed concrete
Coarse particles

CaO/SiO_2 molar ratio = 2



Recycled
Belite Cement Clinker

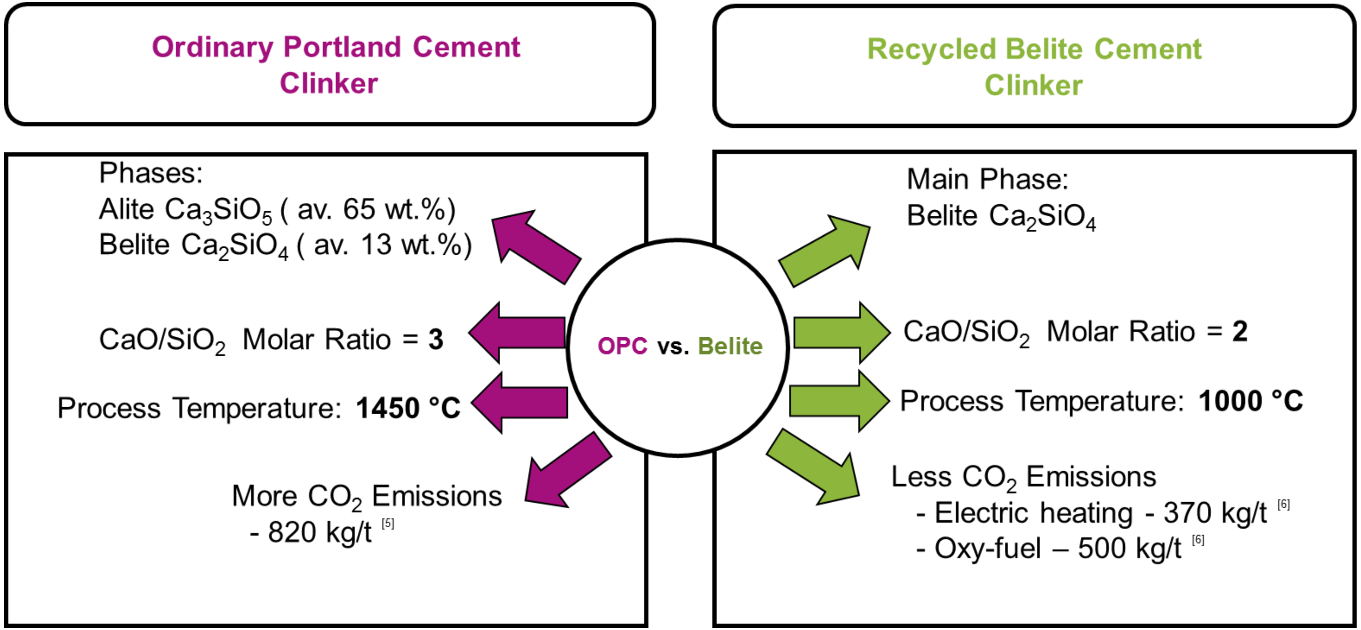
Ordinary Portland Cement (OPC) $CaO-SiO_2-Al_2O_3$ system



Source: Slag Atlas, VDEh 1995

OPC vs Belite

main phase: Alite

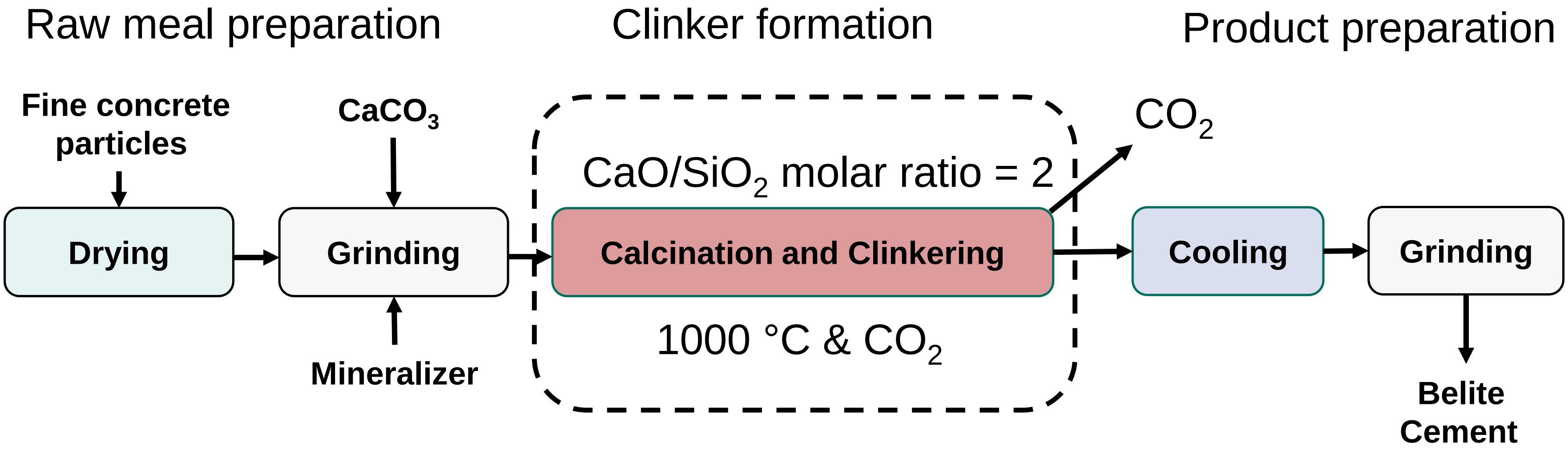


main phase: Belite

slower hydration kinetics

[3] S. Prakasan et al., Study of Energy Use and CO2 Emissions in the Manufacturing of Clinker and Cement, Journal of the Institution of Engineers,2019
[4] P. Stemmermann et al., Recycling belite cement clinker from post-demolition autoclaved aerated concrete – assessing a new process, Resources, Conservation and Recycling 203 (2024)

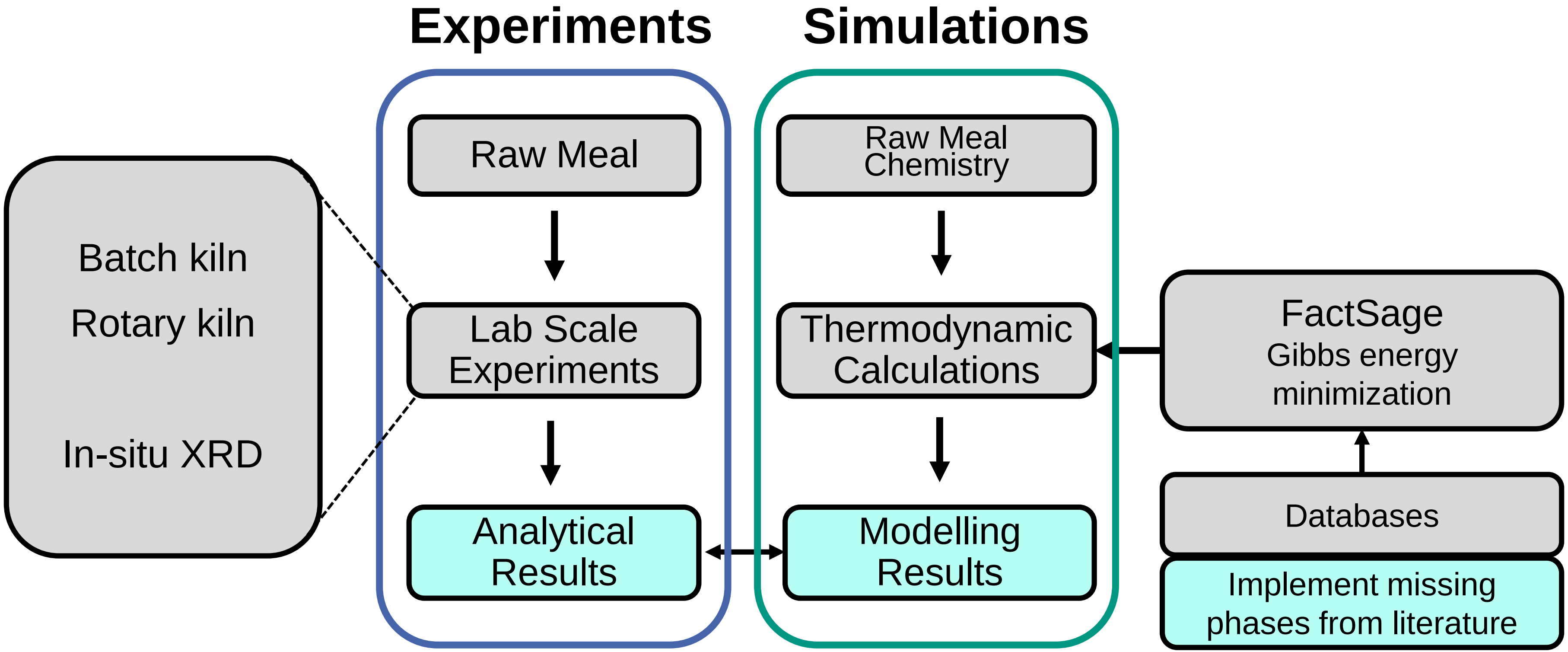
ITC Belite process



Thermodynamic modelling of clinker formation

- Reaction mechanism
- Process conditions
- Intermediate phases, impact of variations

Approach


Experiments
Simulations
Batch kiln
Rotary kiln
In-situ XRD
Raw Meal
Lab Scale Experiments
Analytical Results
Raw Meal Chemistry
Thermodynamic Calculations
Modelling Results
FactSage
Gibbs energy minimization
Databases
Implement missing phases from literature

Results: Simulation at 1000°C

Karlsruhe Institute of Technology

Technical raw meal from AAC waste

Input	wt.%
$CaCO_3$	50.9
SiO_2	23.9
CaO	13.3
$CaSO_4$	3.5
$CaCl_2$	1.7
Al_2O_3	1.6
Fe_2O_3	0.7
MgO	0.6
H_2O	3.8
Total	100

Output

Solid Phases	Simulation (without extensions) wt. %	Experiments wt.%
Belite Ca_2SiO_4	72.2	63.8
Bredigite $Ca_3(Ca, Mg)_4Mg(SiO_4)_4$	11.6	0
Chlorellestadite $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	0	9.9
Wollastonite $CaSiO_3$	2.5	0.6
Melilite $Ca_2(Mg, Fe, Al)(Al, Fe, Si)_2O_7$	9.0	0
Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$	0	3.9
Anhydrite $CaSO_4$	4.7	0
Ternesite $Ca_{10}(SiO_4)_2SO_4$	0	0.1
Lime CaO	0	0.1
Quartz SiO_2	0	2.1
Amorphous Content	0	15.0
Other phases	0	4.5
Total	**100**	**100**

Database extensions

- Factsage Standard Databases
  - FToxid
  - FTsalt

- Cement typical phases that are not part of that
  - Chlorellestadite $Ca_{10}(SiO_4)_3(SO_4)_3(Cl)_2$
  - Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$
  - Ternesite $Ca_5(SiO_4)_2SO_4$
  - Yeelimite $Ca_4Al_6(SO_4)O_{12}$
  - Mayenit $Ca_{12}Al_{14}O_{33}$

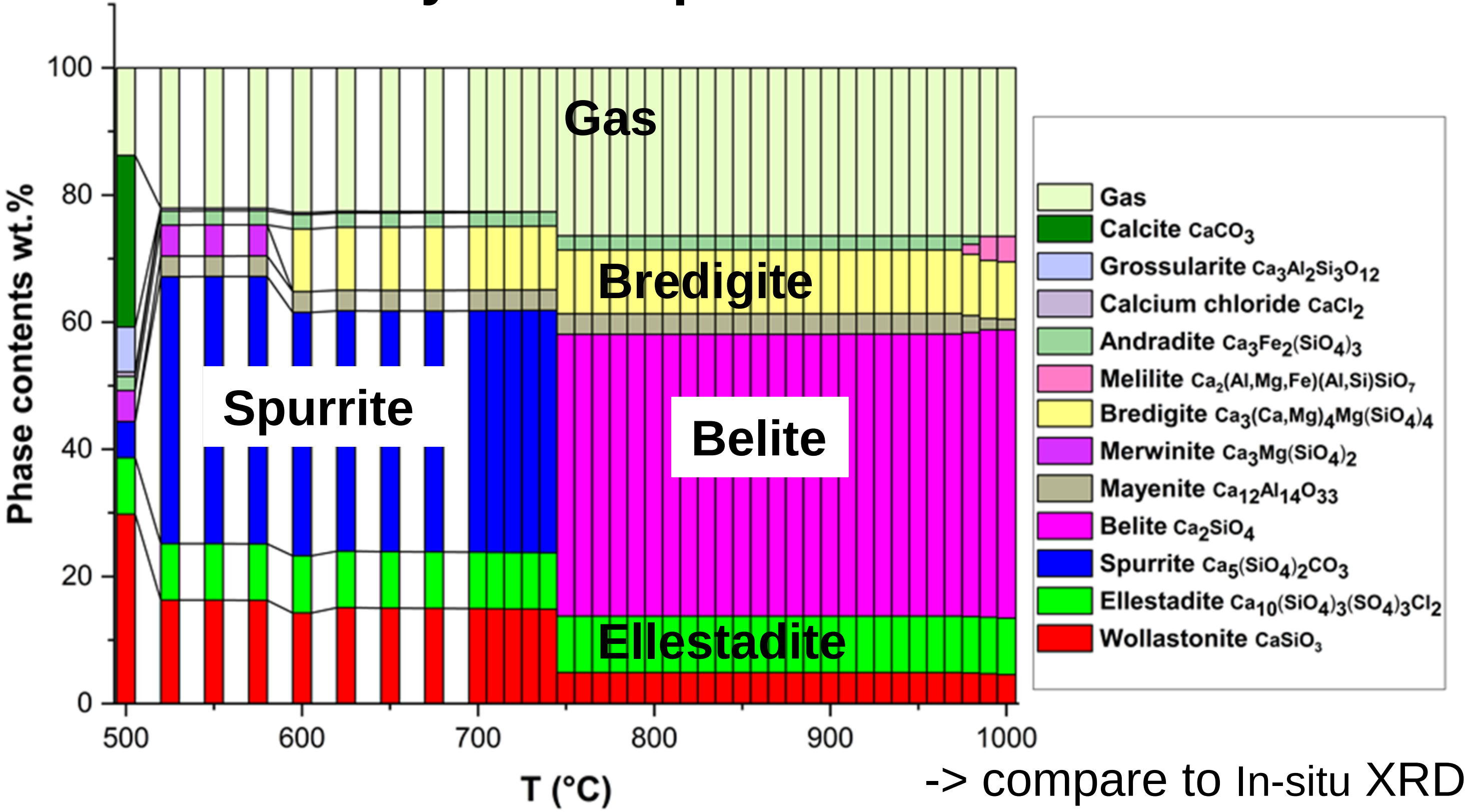
- Implemented as Private Database

Results: Simulation vs Experiments

Karlsruhe Institute of Technology

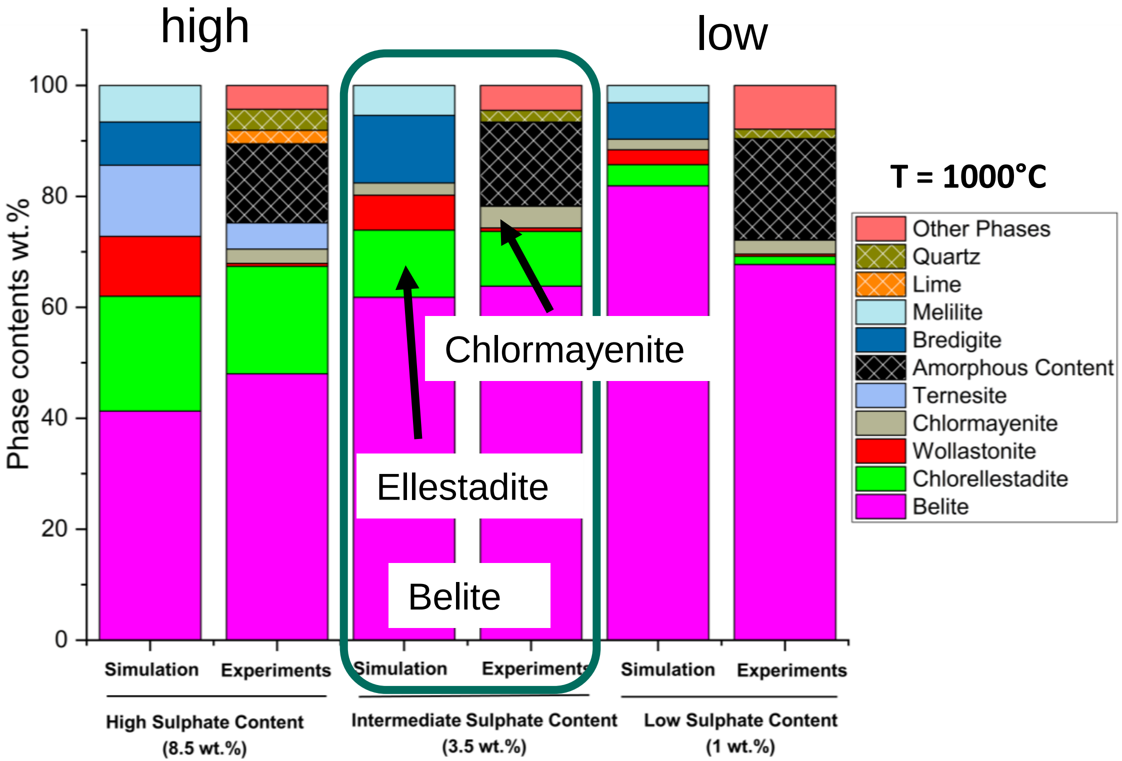
Solid Phases	Simulations (without extensions) wt. %	Simulations (with extensions) wt. %	Experiments wt.%	Comments
Belite Ca_2SiO_4	72.2	61.7	63.8	60% of the solid phase
Bredigite $Ca_3(Ca,Mg)_4Mg(SiO_4)_4$	11.6	12.3	0	Mg
Chlorellestadite $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	0	12.1	9.9	SO_4, Cl
Wollastonite $CaSiO_3$	2.5	6.2	0.6	
Melilite $Ca_2(Mg,Fe,Al)(Al,Fe,Si)_2O_7$	9.0	5.4	0	Mg, Fe, Al
Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$	0	2.3	3.9	Al, Cl
Anhydrite $CaSO_4$	4.7	0	0	
Ternesite $Ca_{10}(SiO_4)_2SO_4$	0	0	0.1	
Lime CaO	0	0	0.1	Grain size, kinetics, inhomogeneity (Lime and Quartz)
Quartz SiO_2	0	0	2.1	
Amorphous Content	0	0	15.0	Real product
Other phases	0	0	4.5	
Total	**100**	**100**	**100**	

Simulation Result: Crystalline phase evaluation



-> compare to In-situ XRD = f(T)

AAC raw meals with different sulfate contents Simulations vs Experiments



Matches

- belite content is approximately the same (deviates between 8 -14 %)
- shows similar (amounts) reservoir elements for chlorine and sulfate
  - Ellestadite $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$
  - Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$

Thermodynamic Modelling Results vs Experiments: On going work

- Raw meal variations
- Experimental differences and imperfections (e.g. unreacted raw meal)
  - Kinetics in solid-solid reactions plus grain size inhomogenities
  - T vs. T profile
  - Gas atmosphere
- Bredigite Ca-Mg silicate: crystallization and/or detection question
- Amorphous content from Q-XRD means X-ray amorphous
  - Thermodynamic calculations yield crystalline phases (and gas phase)
  - Amorphous content could result from melt formation at high T and poor recrystallization or X-ray amorphous products
  - Melt detection and modelling
- Cooling
  - Modelling with Scheil approach
  - Sample quenching with different cooling rates

Summary

Construction waste (fine particles) to Recycled Belite Cement Clinker

- Saves primary resources
- Reduces CO_2 Emissions
- Prevents Landfill

Thermodynamic Modelling

- Understand experiments
- Feedstock variations (AAC, **concrete fines**, waste handling)
- Improve process (scale up) and sample production (applications)

- Model assessment (sensitivity)
- Link kiln model or flow sheet model with FactSage

Thank you for your attention!