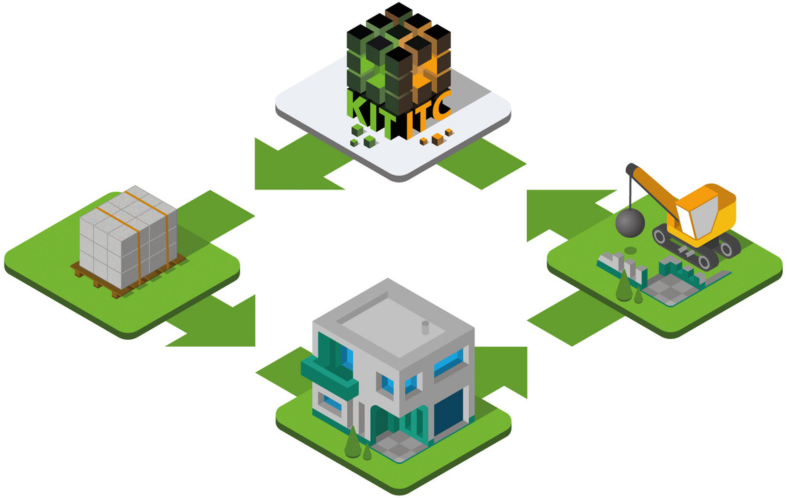
Thermodynamic Modelling of Cement Clinker Formation from Cementitious Waste

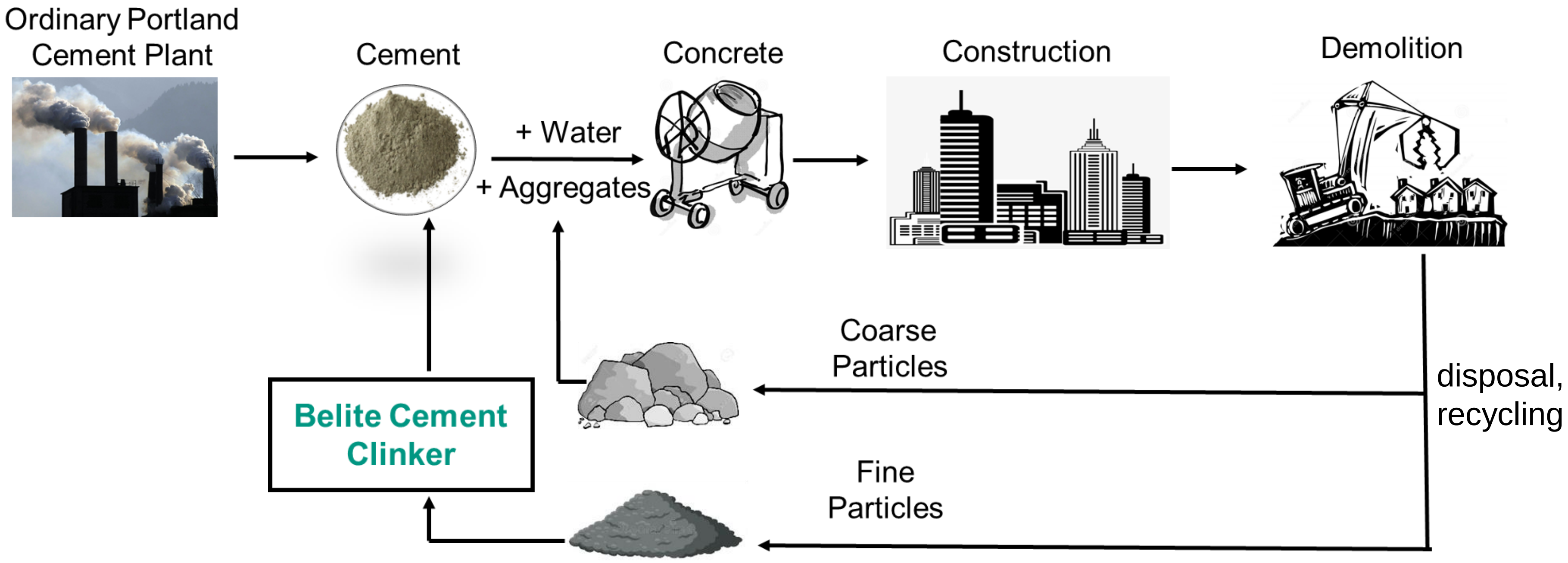
MSE Conference 2024, Darmstadt, September 24th, 2024

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



Circularity in the Cement and Concrete Industry

5-7 % global CO_2 emissions[1]



[1] Laurent Barcelo et al.,Cement and carbon emissions,Materials and structures,2014

Ordinary Portland Cement (OPC) vs Belite Clinker

	OPC	Belite
Raw Materials	Quarry: SiO_2, $CaCO_3$	Concrete Fines: SiO_2 + CaO +$CaCO_3$
CaO/SiO_2 Molar Ratio	3	2
Process	1450°C	1000°C (Mineralizer)
	Fuel combustion	Electric / Oxy-fuel
		CO_2 atmosphere
Main Clinker Phases	Alite Ca_3SiO_5 (~ 65 wt.%) Belite Ca_2SiO_4 (~ 13 wt.%)	Belite Ca_2SiO_4
CO_2 Emissions	~ 820 kg/t [2]	Electric heating - 369 kg/t[3] Oxy-fuel - 501 kg/t[3]

[2] 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
[3] P. Stemmermann et al., Recycling belite cement clinker from post-demolition autoclaved aerated concrete – assessing a new process, Resources, Conservation and Recycling 203 (2024)

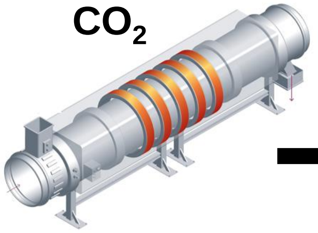
Technical Process and Research Questions

Concrete Fines

+ $CaCO_3$ + Mineralizer (Melt)

some CaO
different sources

T=1000°C
CO_2



Belite Cement Clinker

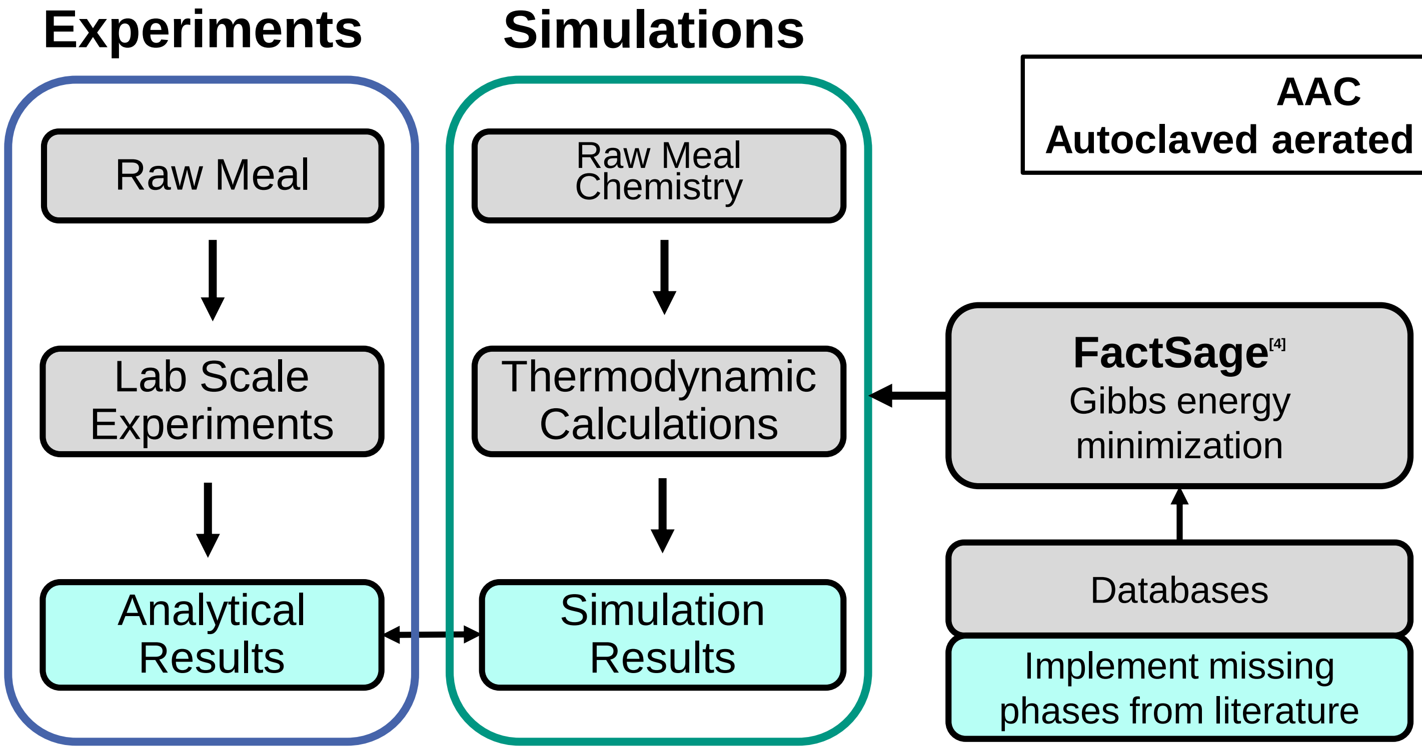
robust process?
scale up?
performance?

- Can thermodynamic simulations minimize the number of experiments?
  - raw meal -> ci, p, T,…-> products
  - variations
- What are reaction principles? Are there intermediate products?
- What are the characteristics of the melt?
- How does the variation of chemical composition effects the product? Optimization?

Approach

Karlsruhe Institute of Technology

AAC
Autoclaved aerated concrete



[4] https://www.factsage.com/

Results: Simulation of Belite Clinker

Input
$CaCl_2$=mineralizer

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

Extensions (Implemented Phases):

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 $Ca_4Al_6(SO_4)O_{12}$
Mayenite $Ca_{12}Al_{14}O_{33}$

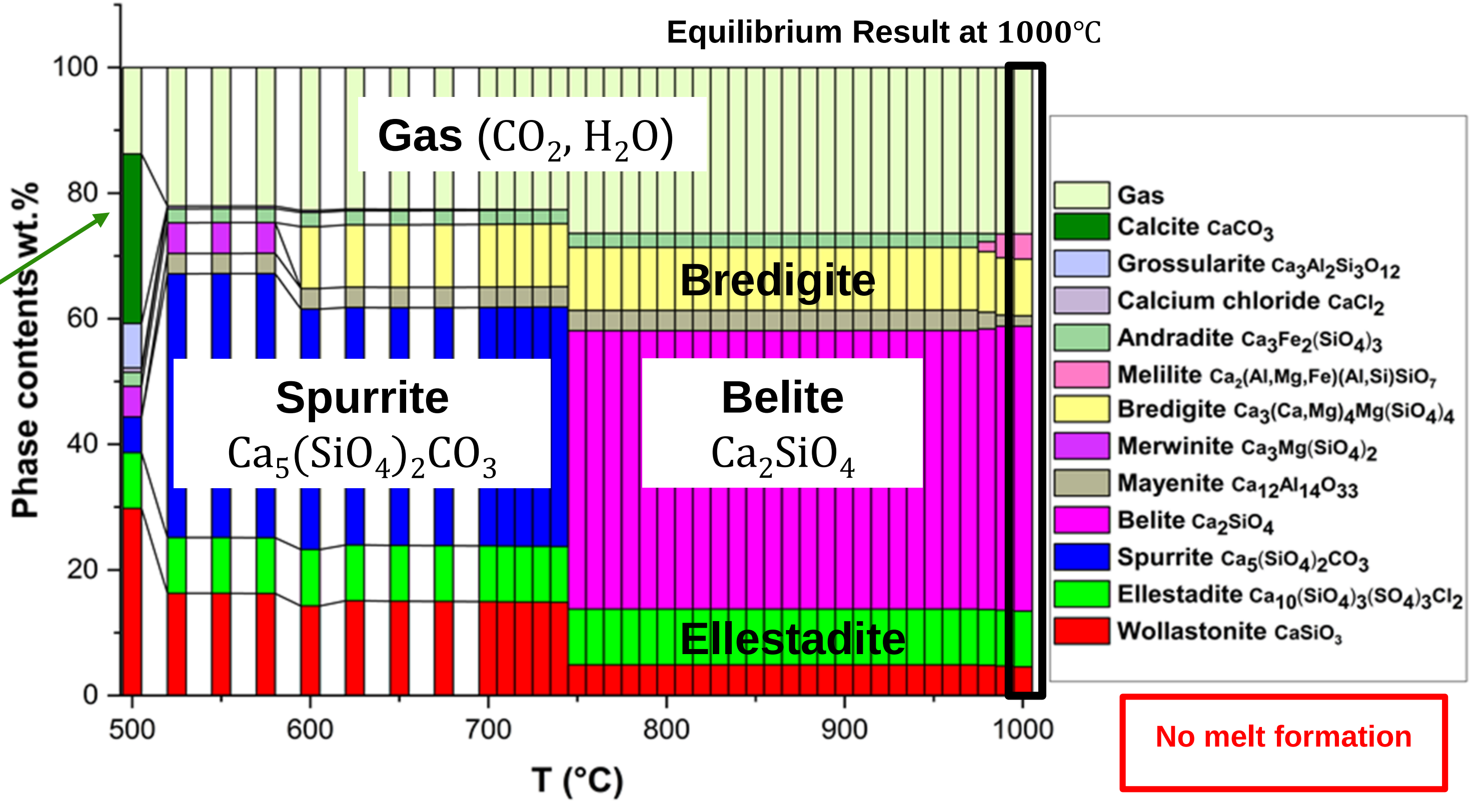
Output
Equilibrium Result at 1000℃

Phases	wt. %	
Belite Ca_2SiO_4	45.4	Exp. ~46 wt.%
Bredigite $Ca_3(Ca, Mg)_4Mg(SiO_4)_4$	9.0	
Chlorellestadite $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$	8.9	Exp. ~8 wt.%
Wollastonite $CaSiO_3$	4.6	
Melilite $Ca_2(Mg, Fe, Al)(Al, Fe, Si)_2O_7$	4.0	
Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$	1.7	
Gas (CO_2 and H_2O)	26.4	
Total	100	

Results: Crystalline Phase Evaluation of Simulations

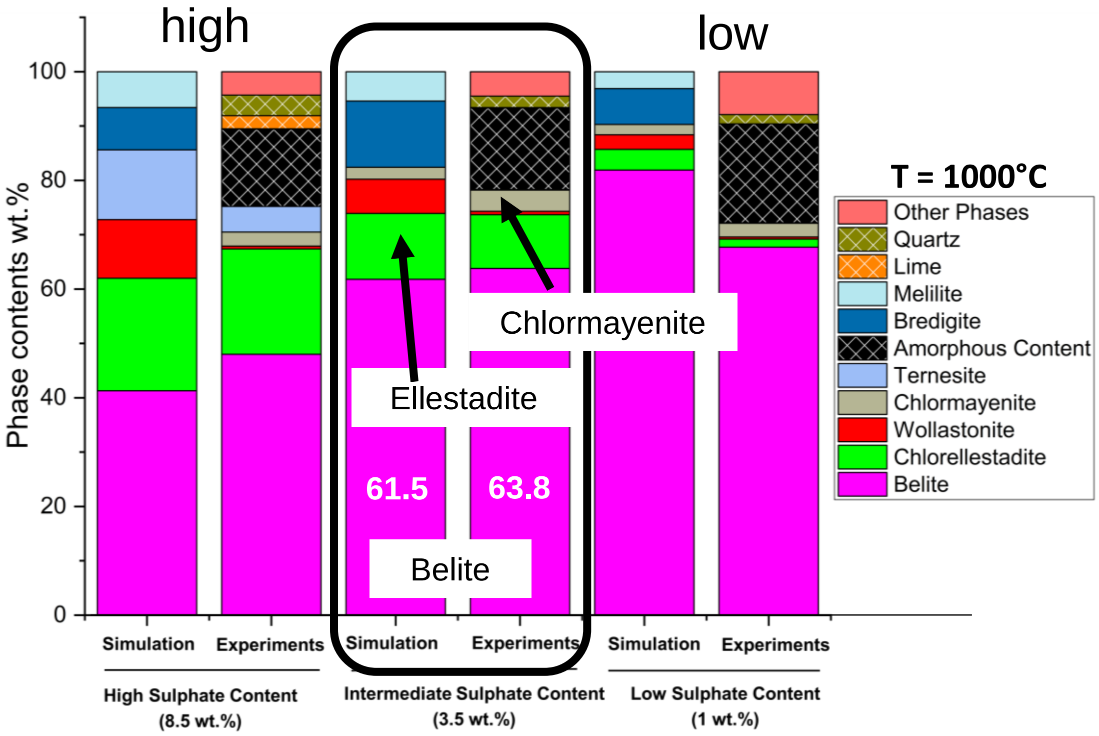
Karlsruhe Institute of Technology

Calcium Carbonate $CaCO_3$



No melt formation

Simulations vs Experiments
AAC Raw Meals with Different Sulphate Contents



1. Belite contents fit well for all raw meals
2. Reservoir minerals for chlorine and sulphate match

   Ellestadite $Ca_{10}(SiO_4)_3(SO_4)_3Cl_2$

   Chlormayenite $Ca_{12}Al_{14}Cl_2O_{32}$

3. Poorly crystalline Bredigite

   XRD detection constraints

4. Incomplete conversion of Lime and Quartz

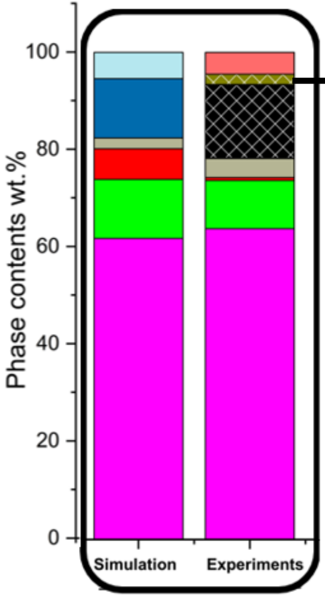
   Grain sizes, Mixing, …

5. Typical Amorphous Content (10-20 wt.%)

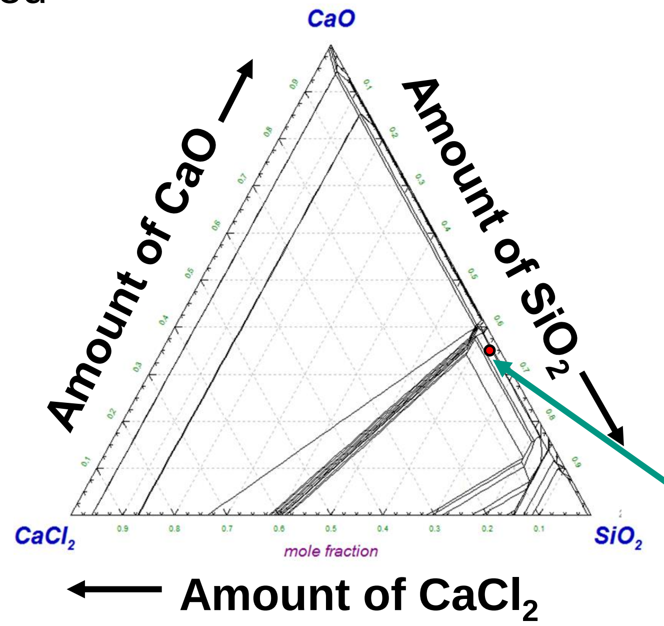
   XRD: only Quantity, Crystallization/Melt

Simulation- Phase Diagram at 1000°C
AAC Raw Meal with Intermediate Sulphate Content

Composition of the complex oxide system in ternary phase diagram



Unreacted SiO_2

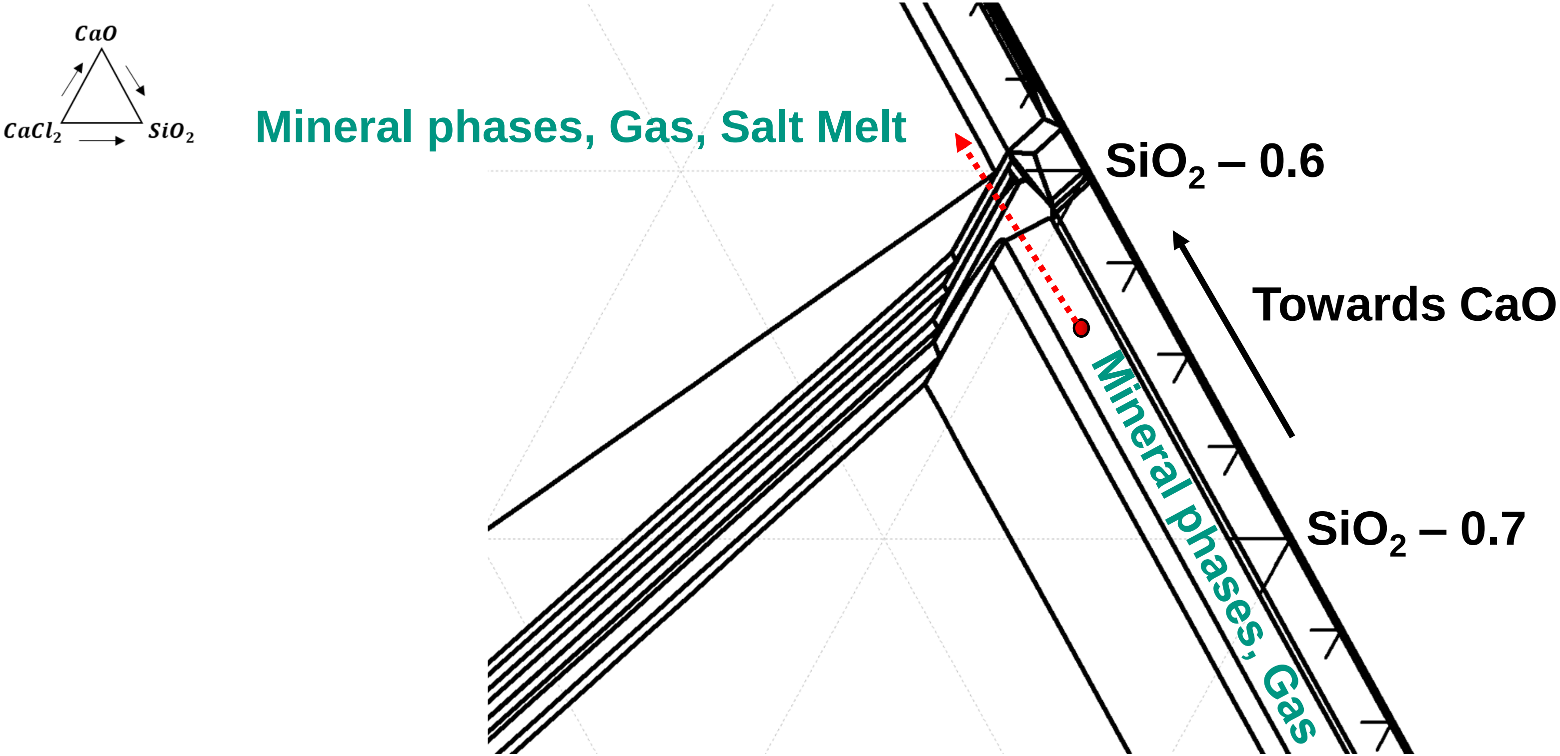


Minor Components
Al_2O_3,$CaSO_4$ Fe_2O_3,
MgO, $CaCO_3$,H_2O

Raw Meal composition

[4] https://www.factsage.com/

Simulation- Phase Diagram at 1000°C
AAC Raw Meal with Intermediate Sulphate Content



Summary and Outlook

Thermodynamic Simulations for Belite Process work

- Complex Raw Meals
- Major Reactions
  - Gas Phases and Intermediate Products
- Technical and Variable Raw Meals
  - Prediction of Belite
  - Chlorine and Sulphate -> Reservoir Mineral Ellestadite, less Belite
  - Mg, Al, Fe

Future work

- Concrete Fines from Waste Concrete
- Melt: Formation Temperature, Composition (Carbonate Melts) -> DSC, Heating Microscopy, SEM, Raman
- Mineralizer: different types and additions, combinations
- Experimental constraints: amorphous content

Thank you for your attention!

Pallavi Reddy Yarka Reddy M.Sc.

Karlsruhe Institute of Technology (KIT)
Institute for Technical Chemistry (ITC)

Hermann-von-Helmholtz-Platz 1
76344, Eggenstein Leopoldshafen, Germany

E-mail: pallavi.reddy@kit.edu