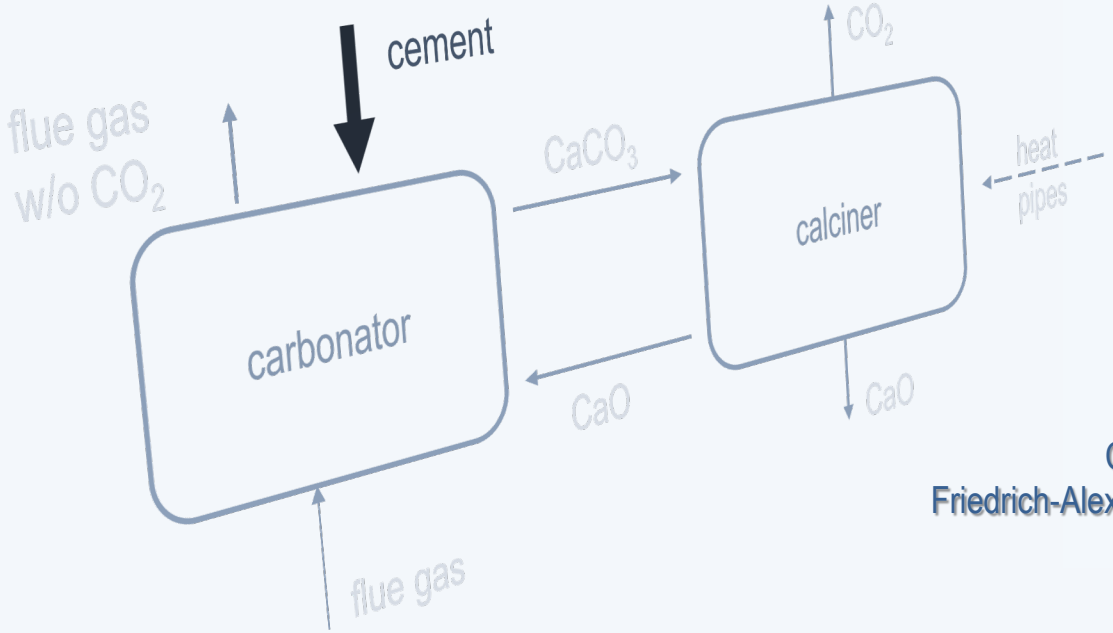
ACT Project ANICA
Advanced Indirectly Heated
Carbonate Looping Process

Experimental Characterization of Cement Raw Meal for Application in the IHCal Process

06.10.2021



Kyra Böge

Prof. Dr.-Ing. Jürgen Karl
Chair of Energy Process Engineering
Friedrich-Alexander University Erlangen-Nürnberg
Fürther Str. 244f, 90429 Nürnberg
Email: kyra.kb.boege@fau.de

FRIEDRICH-ALEXANDER UNIVERSITÄT ERLANGEN-NÜRNBERG
TECHNISCHE FAKULTÄT

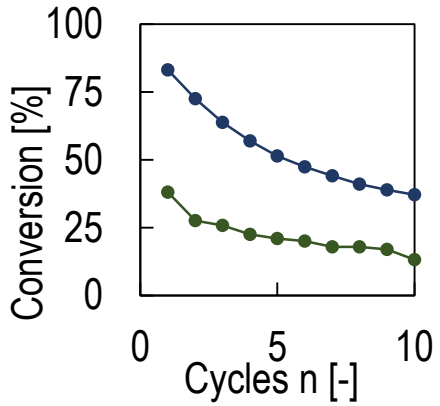
Challenges with cement raw meal

Inorganic components form several material phases of cement raw meal interact with lime

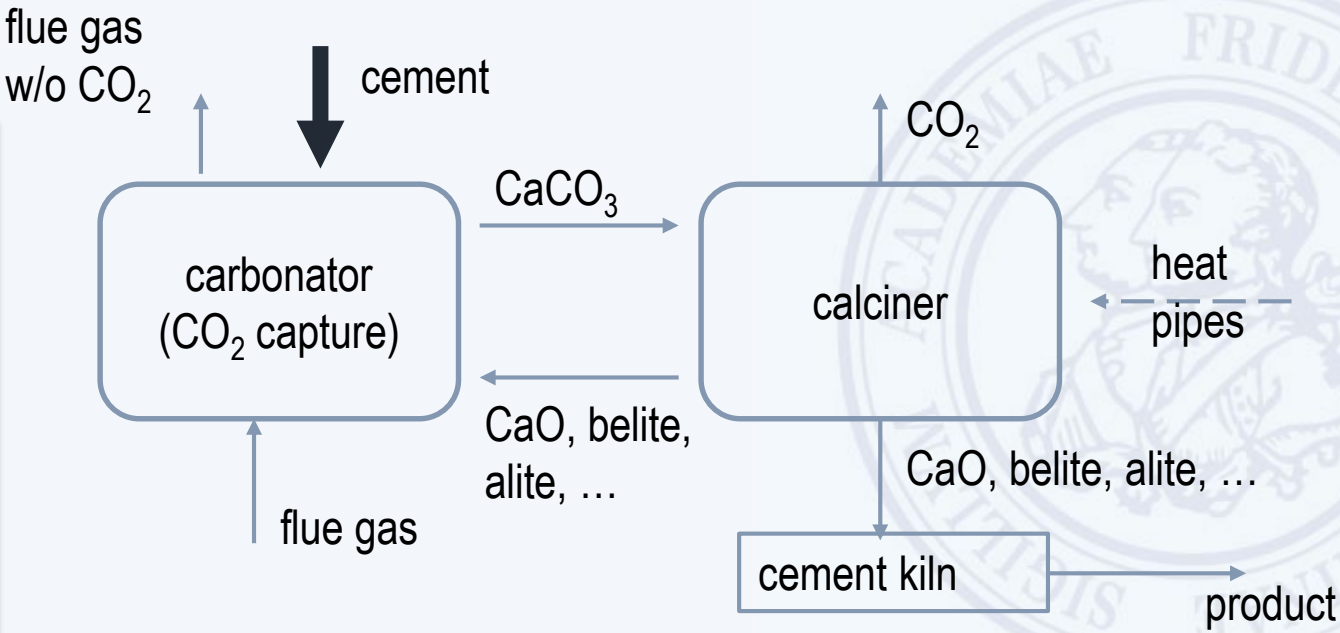
- How will this effect influence the behaviour of the carbonation?
- Will such a pre-treated cement meet the high quality standards of the cement industry?

Phase formation

Reactivity



Cyclic conversion of **lime** and **cement raw meal** during carbonation

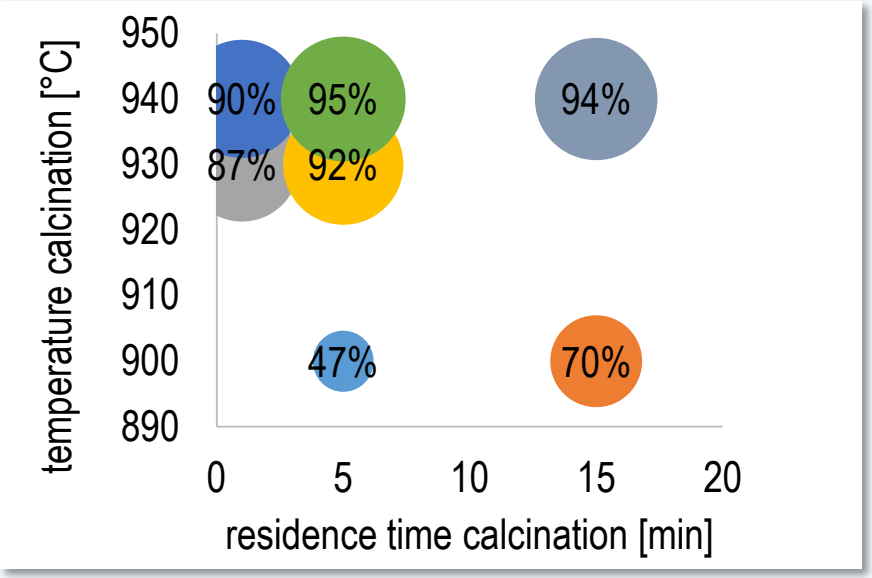


Reactivity

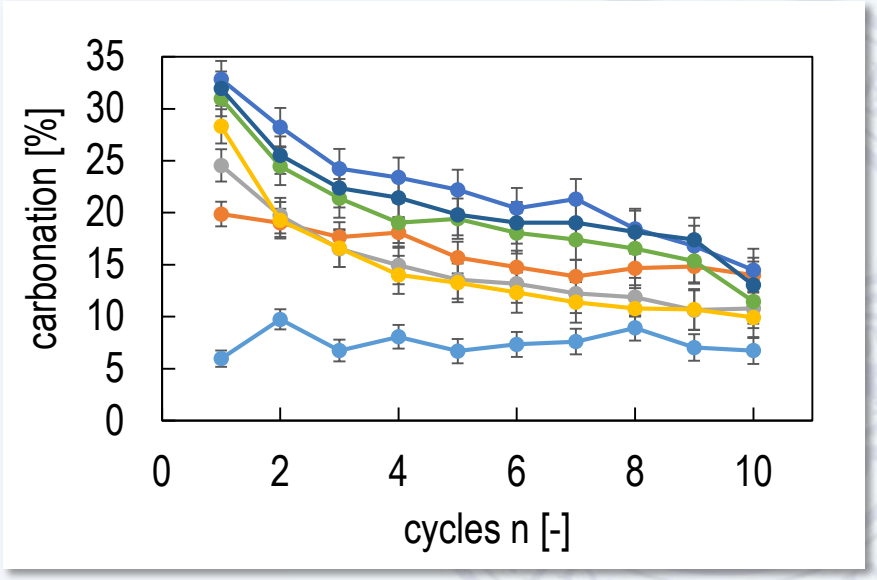
Reactivity TGA Tests

"Can the phase formation be avoided by calcination at low temperatures and short residence times during calcination?"

Conversion (**calcination ≙ CO_2 release)** at different temperatures and residence times during **calcination**



Conversion rate during **carbonation** comparable carbonation conditions: 650 °C; 100 % CO_2; 15 min residence time

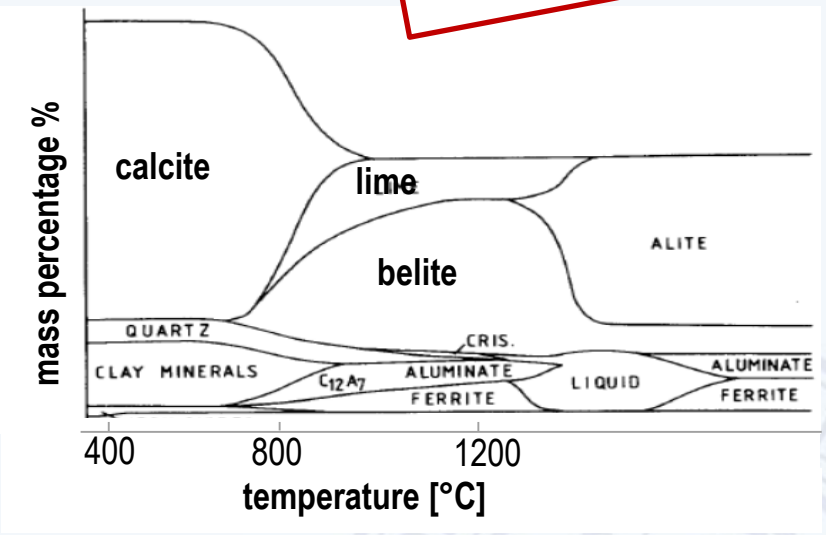


- Highest conversion of calcination and carbonation at highest temperatures probably due to increased availability of free-lime
- Assumption: long residence times (longer than 5 min) and slow heat rates lead to phase formation which will either limit the reactivity or the availability of free-lime

Phase formation

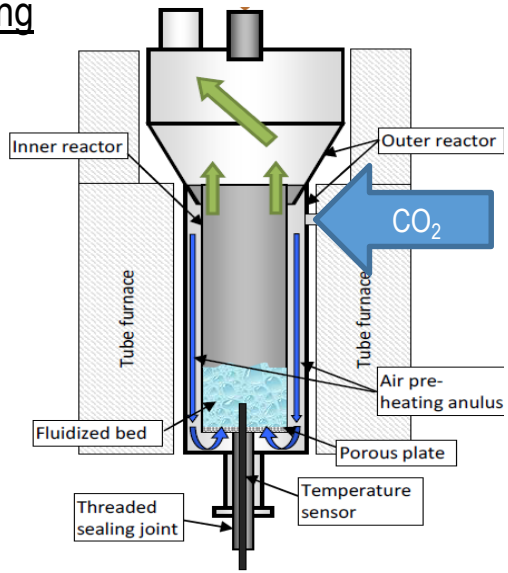
Phase formation

- Phase formation is a function of temperature and the residence time of cement raw meal (thermodynamically equilibrium)
- **Key question:** Is the product quality of cement affected by cement raw meal used in the carbonate looping process with its specific pre-treatment?



Cement raw meal contains several inorganic components which can form different material phases in the product depending on process temperature and duration

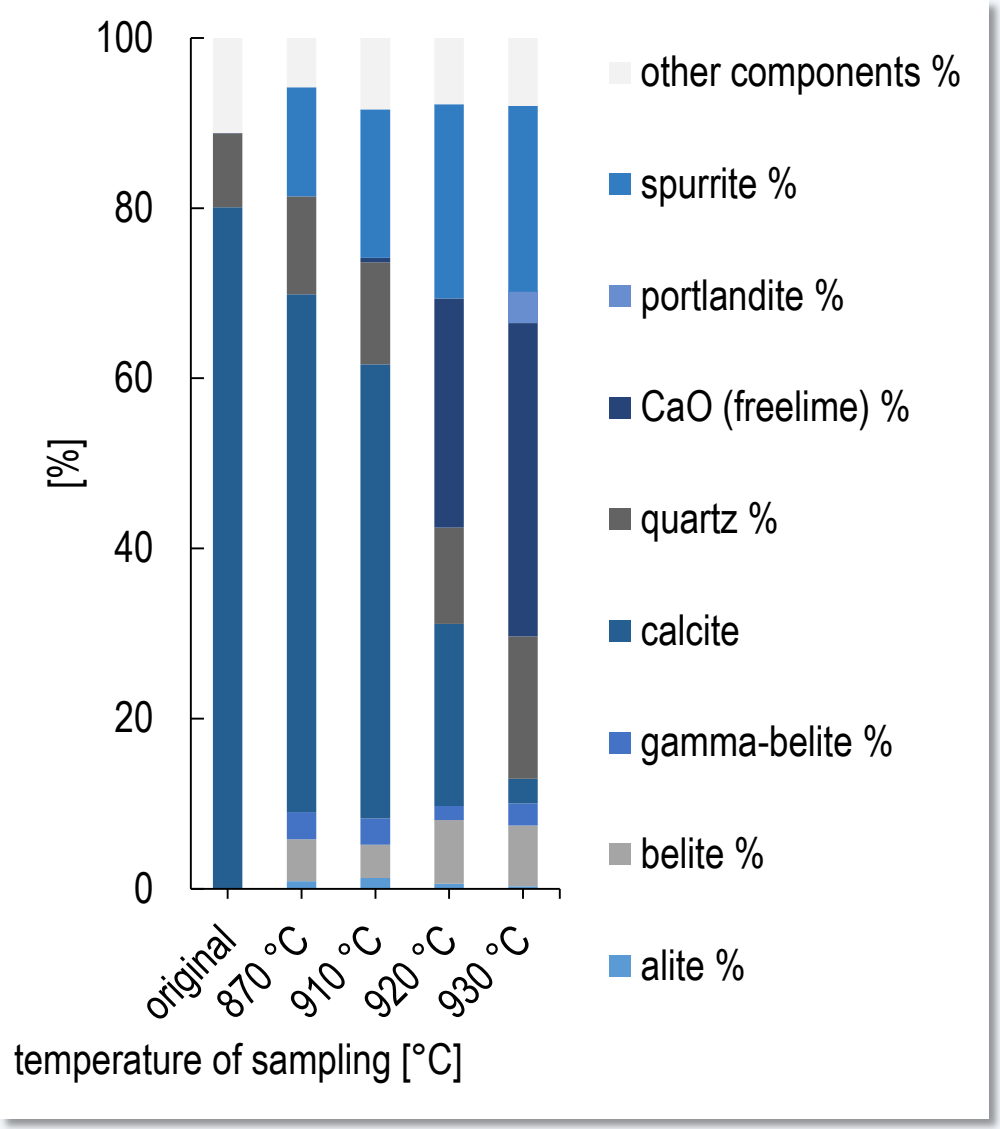
Fluidized bed with optical access for sampling



- Investigation of the phase formation and the influence on the product quality in order to clarify the reasons why the reactivity of cement raw meal and CO_2 is low in comparison with limestone
- Fluidisation of cement raw meal with CO_2 and sampling of cement raw meal during the experiment and analysis by Dyckerhoff

Phase formation

Phase formation during heating up



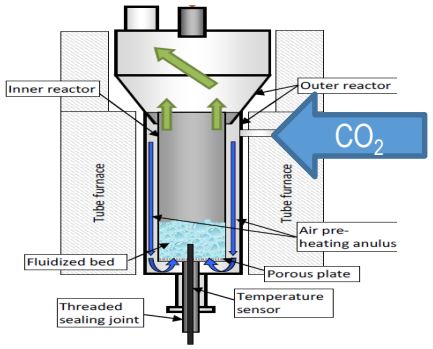
Change of material phases during calcination

- Free-lime (CaO) available at temperatures higher than 920 °C
- γ-belite is formed in a temperature range above 870 °C
- Belite formation can not be avoided in this fluidized bed calcination!
- Total belite content is approximately between 8-10 %
- Spurrite content increases with the temperature from 13 % at 870 °C to 22 % at temperatures of 920-930 °C
- According to literature[*]:
  - Spurrite will decompose at temperatures higher than 950 °C
  - It is still not clear whether this will lead to increased belite formation and its influence on the availability of CaO

[*] cement chemistry by Taylor

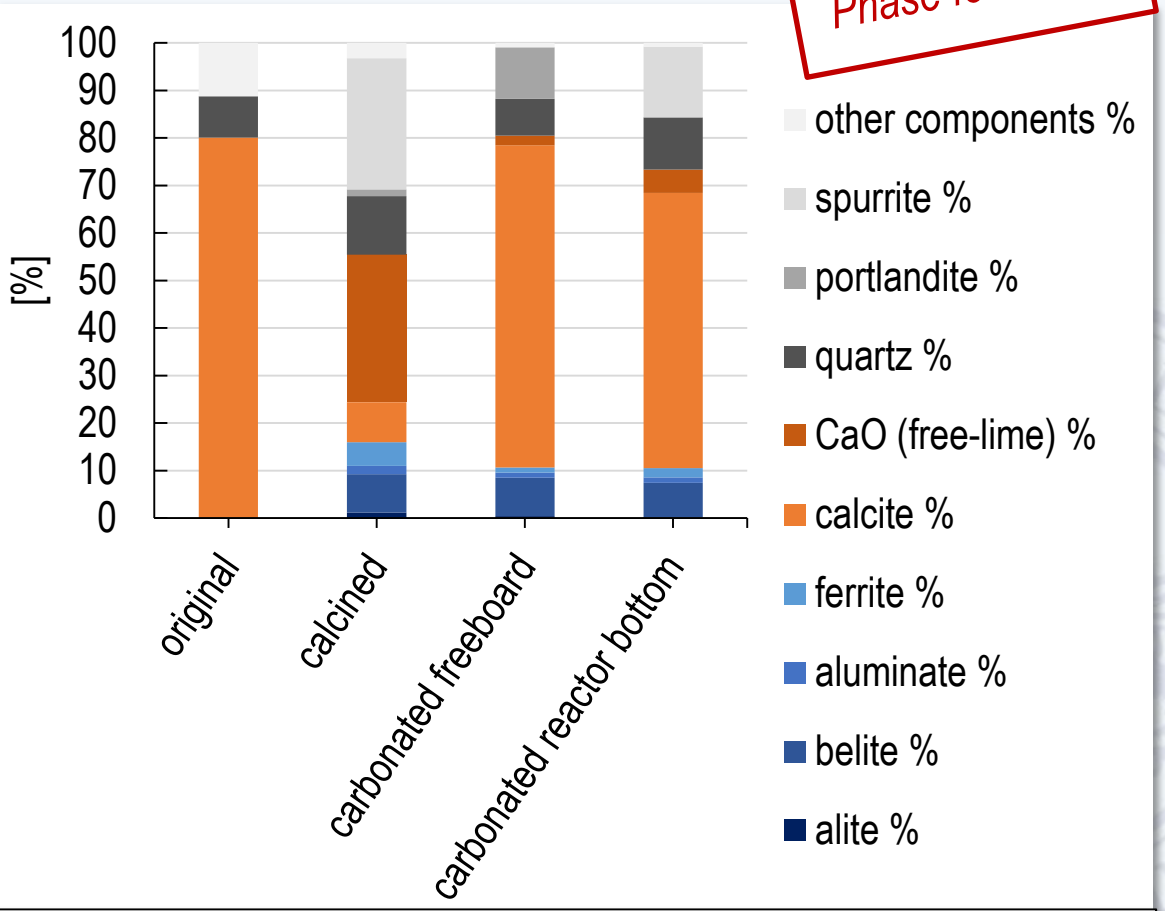
Phase formation during calcination and carbonation

Fluidized bed with optical access for sampling



Sampling of cement raw meal during calcination at 930 °C and at the end of a calcination and carbonation cycle from the reactor freeboard and the reactor bottom

Phase formation

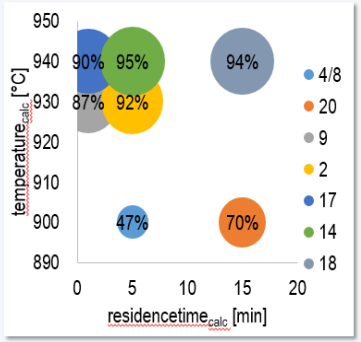


- CaO (free-lime)/ $CaCO_3$ (calcite) content increases and decreases with the calcination and carbonation reaction
- Formation of clinker phases (alite, belite, aluminate, ferrite) starts already during the calcination and carbonation cycles
- Unexpected amounts of clinker phases portlandite and spurrite

Phase formation on the behaviour of the carbonation?

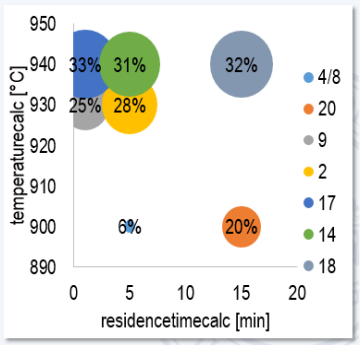
Reactivity

Conversion of **calcination** at different temperatures and residence times of **calcination**

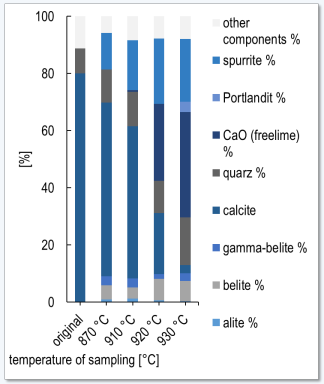


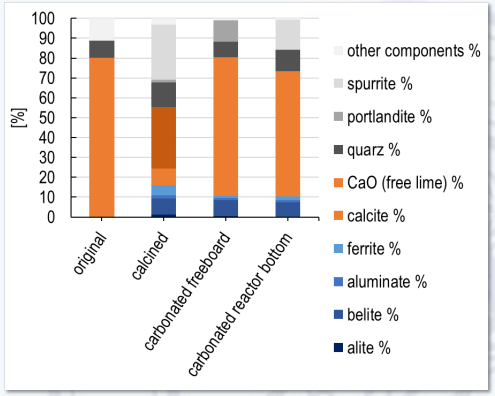
Same carbonation conditions: 650 °C; 100 % CO2; 15 min residence time

Conversion of **carbonation** at different temperatures and residence times of **calcination**



Phase formation





- Low reactivity (only 30 % conversion rate) of cement raw meal and CO_2 in comparison with limestone
- Low calcination rates at 900 °C requires elevated temperatures

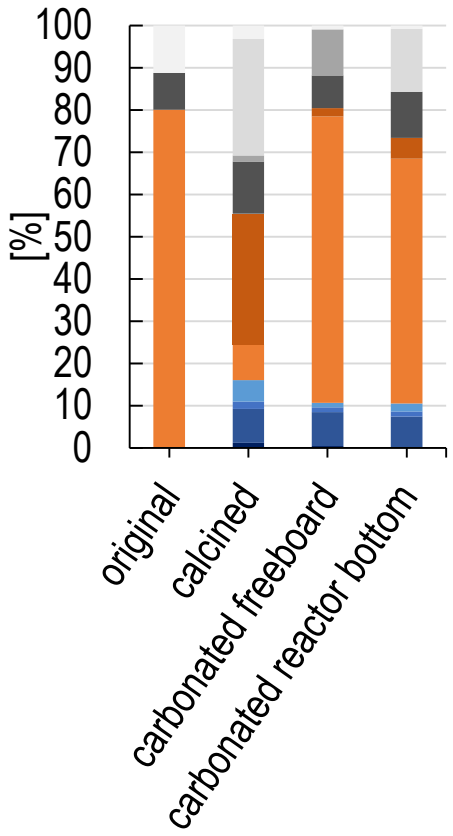
- Belite & spurrite formation as well as other clinker phases limiting the content of CaO (free-lime)/ $CaCO_3$ (calcite)
- CaO available at temperatures above 920 °C
- $CaO/CaCO_3$ content increases and decreases with the calcination and carbonation reaction

Formation of belite and spurrite decreases the conversion rate and the reactivity of cement raw material in the IHCaL-process
=> Will such a pre-treated cement meet the high quality standards of the cement industry?

Investigation of the phases on the product quality

Phase formation

Pre-treated (calcination and carbonation) cement raw meal in a fluidized bed

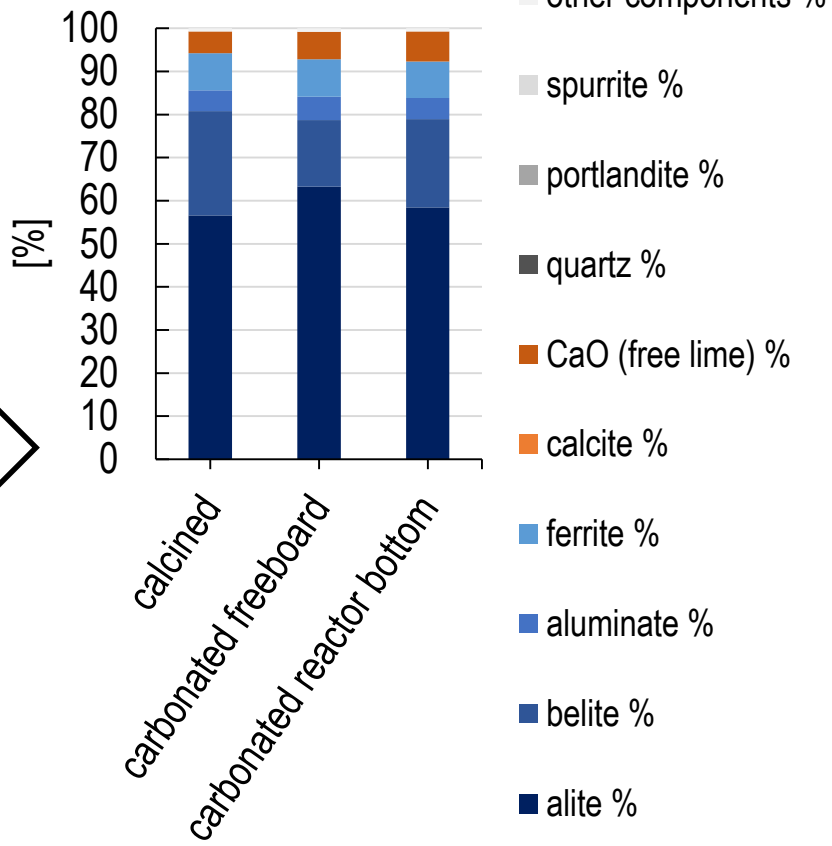


75 % original cement raw meal + 25 % sample meal

Dyckerhoff

Burned at 1450 °C for 45 min at laboratory scale

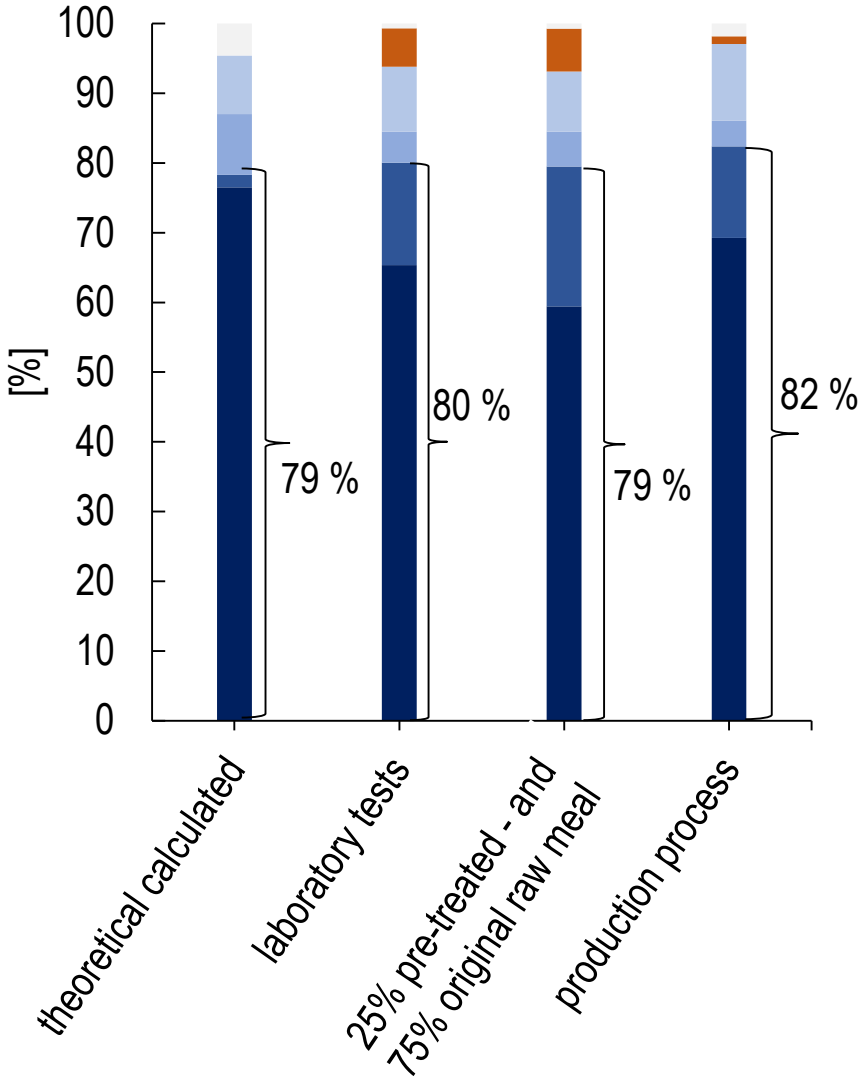
25 % pre-treated- and 75 % untreated cement raw meal



- Quartz, portlandite and spurrite decompose at high temperatures
- Still an unwanted free-lime content 5-7 % is available
- The amount of clinker phases (alite, belite, aluminate, ferrite) increased

Classification of the results

Phase formation



- Difference in the results of laboratory tests with the results of material of the production process explainable through missing scale-up parameters and non-existing reactions with fuel in the cement oven
- Existing free-lime reacts with fuel in the cement oven, further tests should consider a lower lime standard which consider these reactions
- Compliance with the cement standard that the sum of belite and alite surpass 75 %
- Consisting quartz in the cement raw meal completely reacted to clinker phases, this is an indication that the clinker phase formation is completed

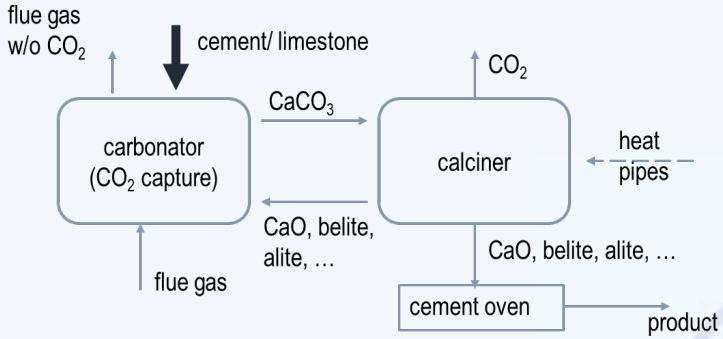
Challenges with cement raw meal

Inorganic components form several material phases of cement raw meal interact with lime

Reactivity

How will this effect influence the behaviour of the carbonation?

- Reactivity tests show acceptable conversion during carbonation and calcination with an averaged conversion of 20 %
- Clinker phase formation as a reason for low reactivity in comparison with pure lime
- Further tests need to be carried out for further optimization



Phase formation

Will such a pre-treated cement meets the high quality standards of the cement industry?

- Pre-treated cement raw meal meets the high quality standard of the cement industry, consisting 75 % clinker phase of belite and alite
- Unwanted phases in pre-treated meal (spurrite and portlandite) react to clinker phases
- A free-lime content higher than 7 % is lead back to differences between the laboratory and real case application