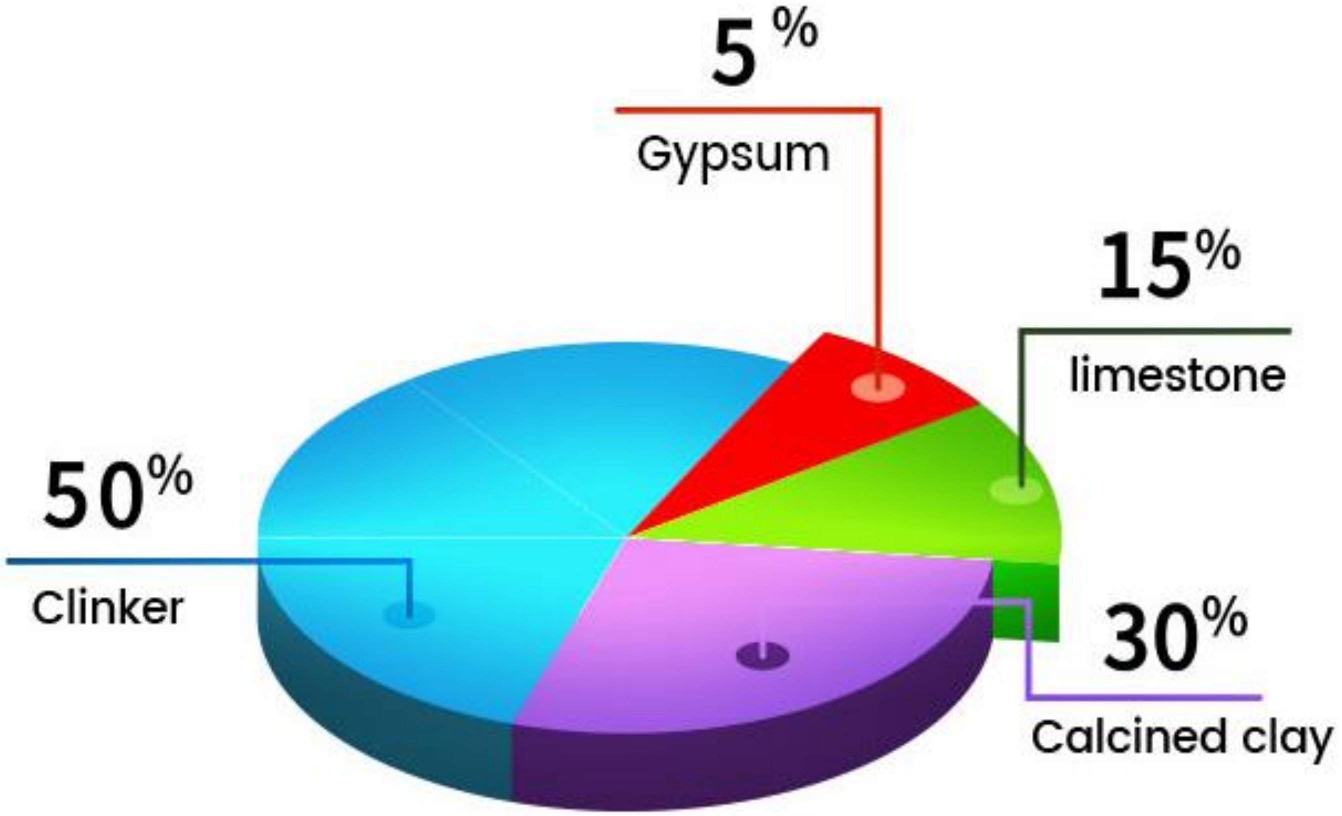
58. Aachener Baustofftag, 22.03.2022, Aachen

# Early Hydration and Rheology of Limestone Calcined Clay Cements

Tafadzwa Ronald Muzenda, M.Sc.

Institut für Baustoffforschung (ibac)

# From OPC to limestone calcined clay cement

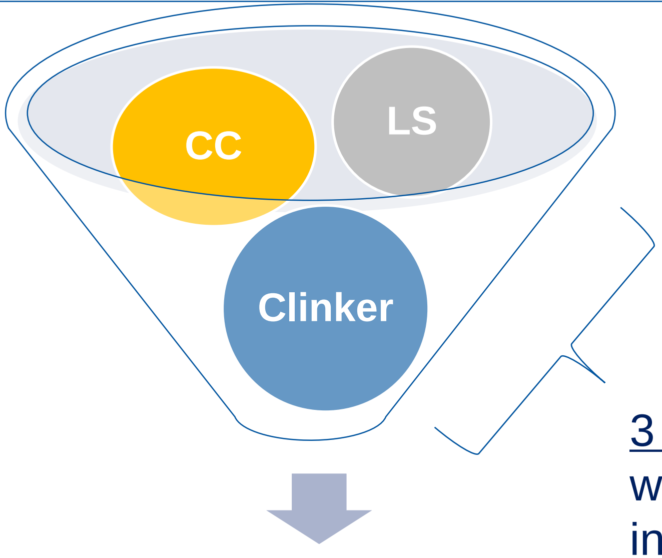



- Clay containing kaolinite is **abundantly available** in the earth's crust and when calcined and used together with limestone, **it yields comparable physiochemical properties and better durability** when compared with pure OPC even at 50% clinker substitution.

- Advantages of limestone calcined clay cement:
  - ❑ Lower carbon footprint
  - ❑ Superior durability
  - ❑ Lower cost

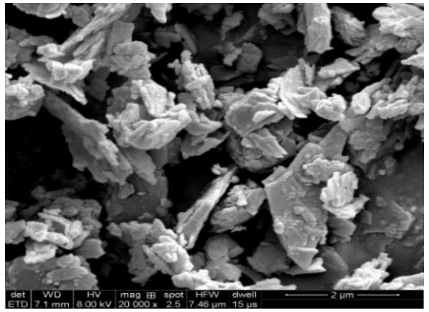
*(lc3.ch)*
*(lc3trcindia.com)*

# Questions on the rheology of limestone calcined clay cement

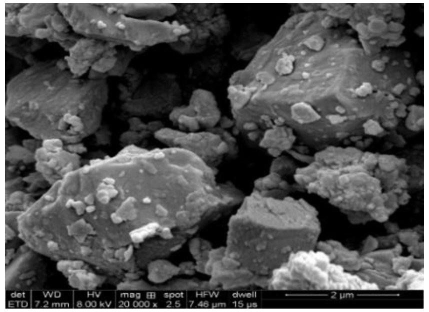



**Limestone-calcined clay cement**

<u>3 main components</u> with considerably varying inherent <u>rheological properties.</u>



Calcined clay

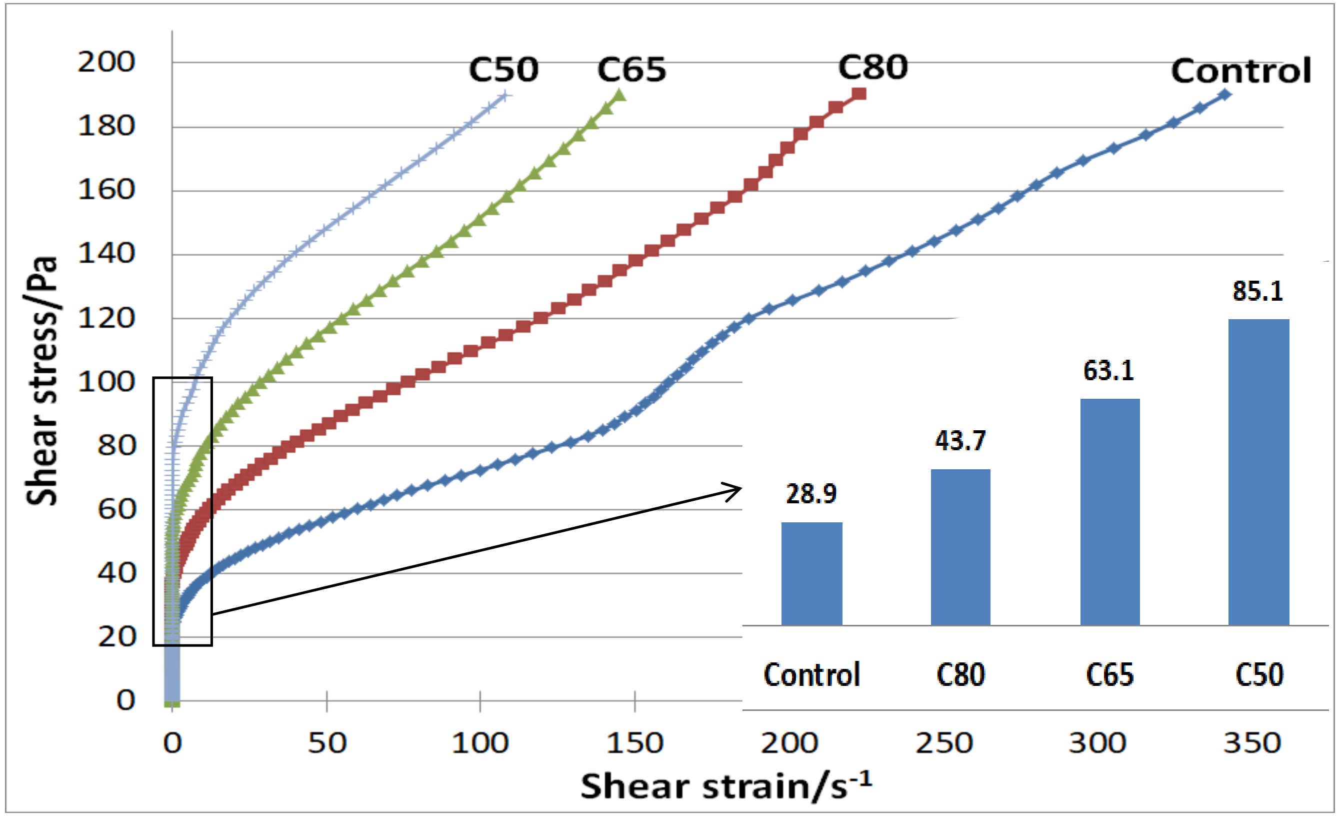


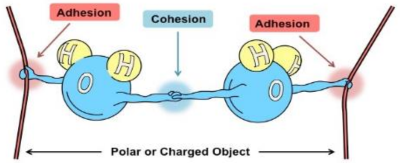
Limestone

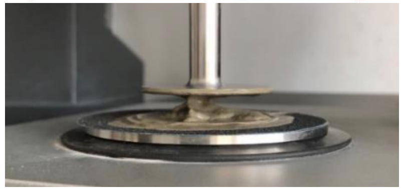
**Questions:**

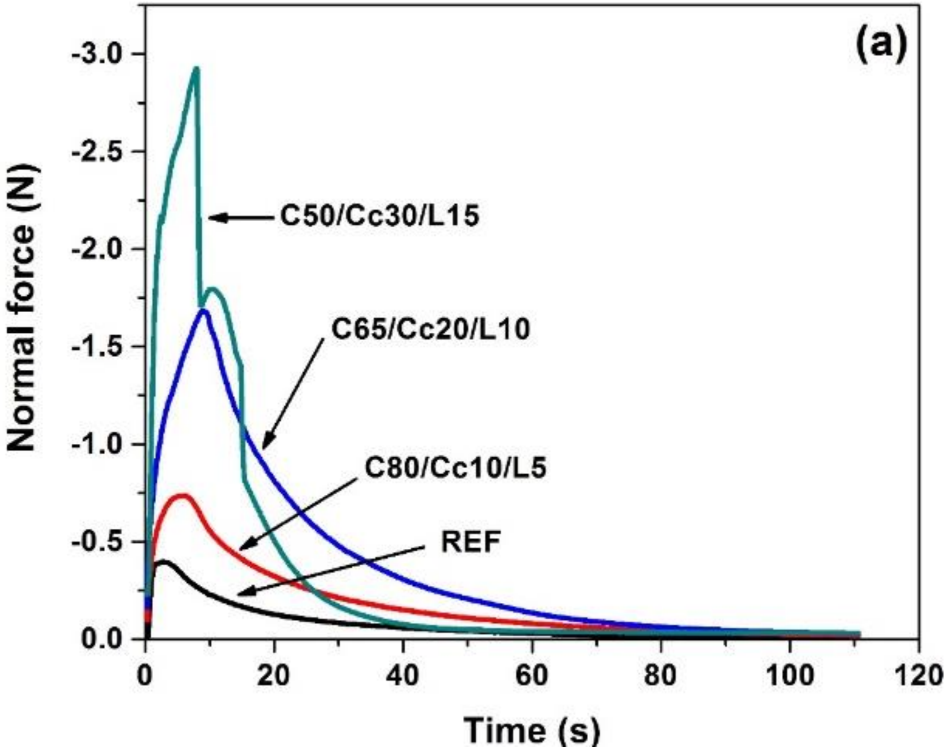
1. Combined effect of calcined clay and limestone? Independent effect?
2. Origin of thixotropic buildup and the influence of the physiochemical properties of clay?
3. Effect of clay secondary phases and impurities?

# Rheology differences between OPC and limestone calcined clay cements



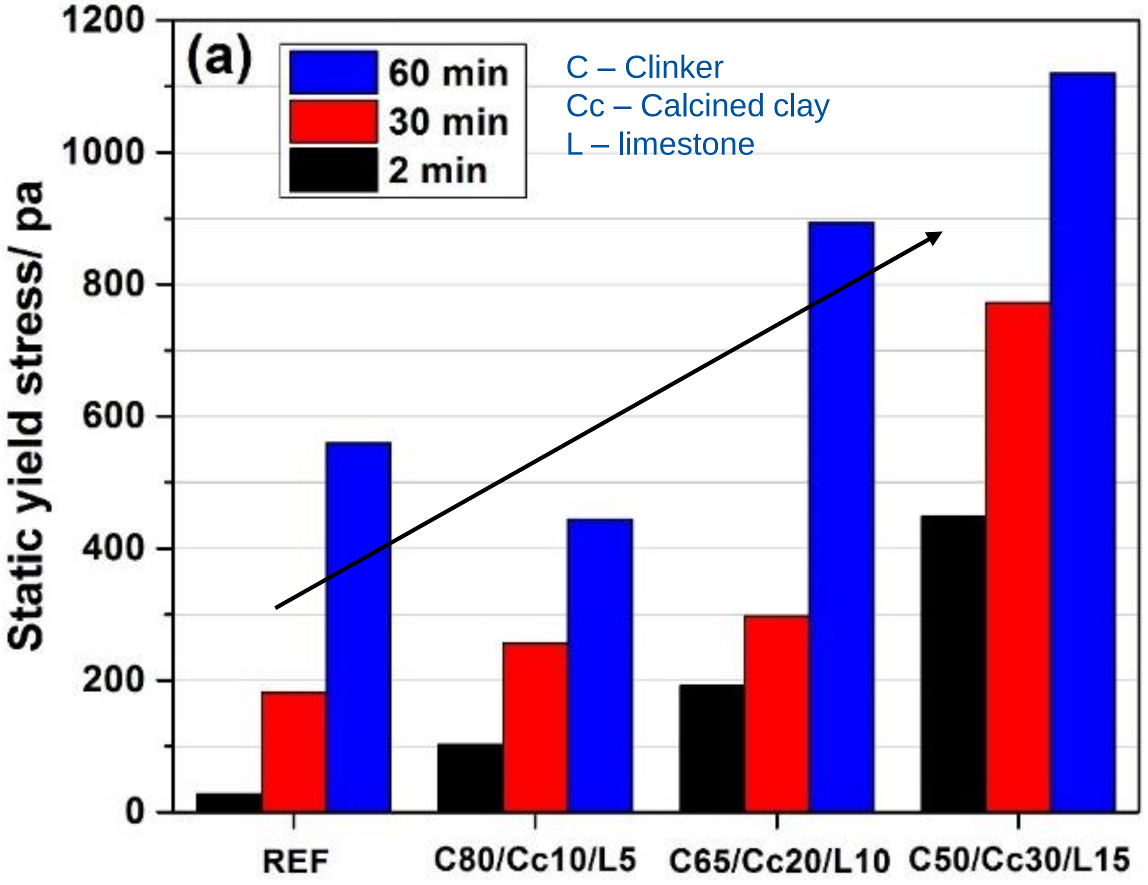



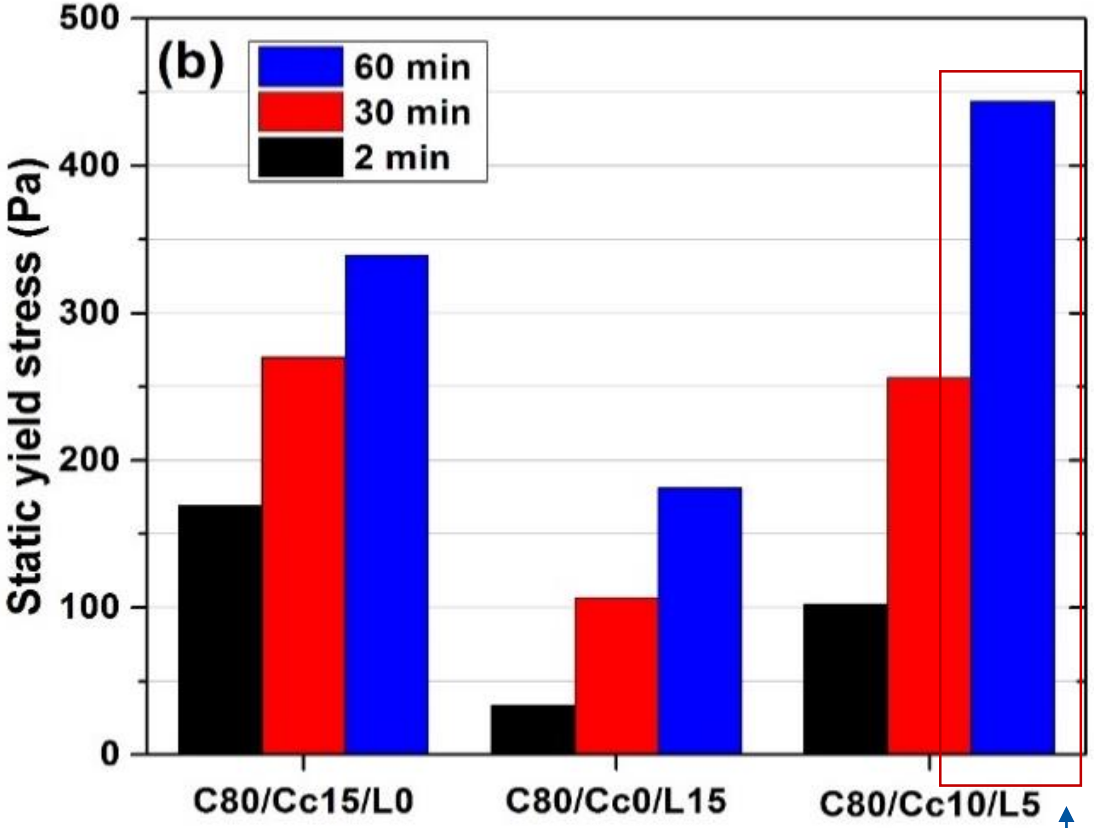






- ❖ Increase in SCM content leads to increase in static yield stress, viscosity, cohesion as well as thixotropic buildup.

# Role of limestone and calcined clay in the rheology of limestone calcined clay cements




*Calcined clay effect*

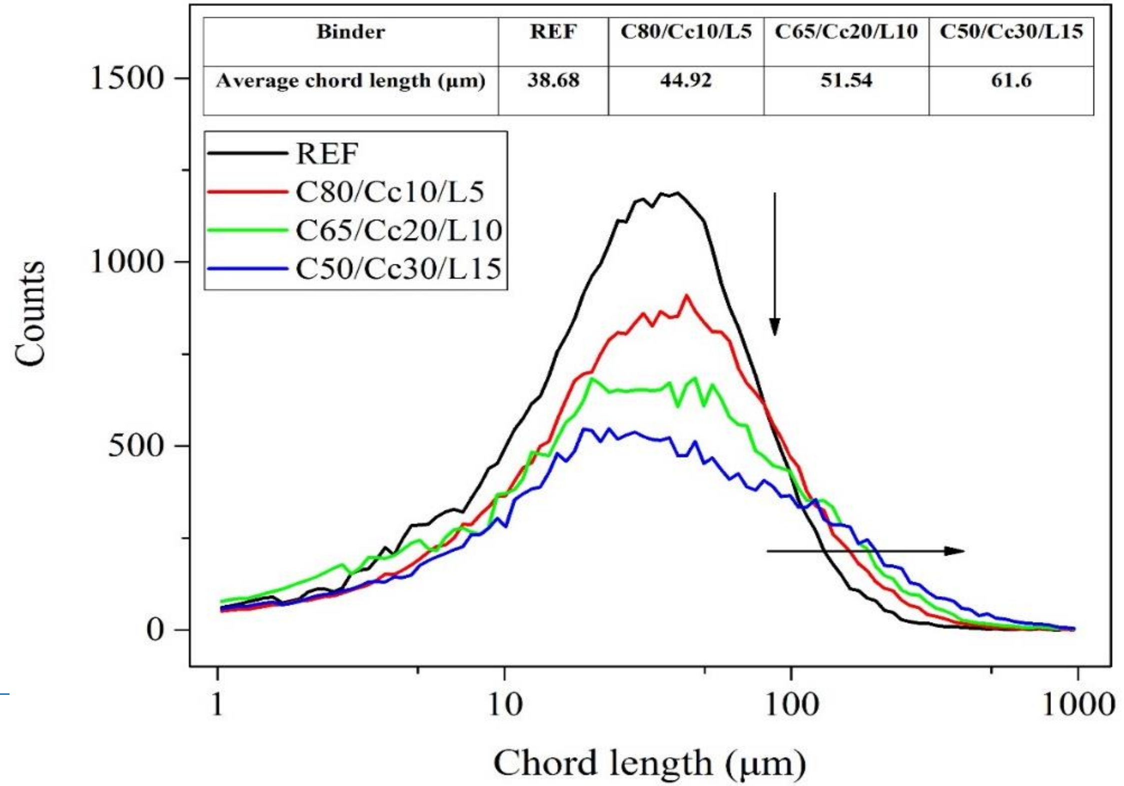
*Limestone effect*

**Hydration synergy at 60 min** in system with both limestone and calcined clay.

*(Muzenda et al, CCC, 2020)*

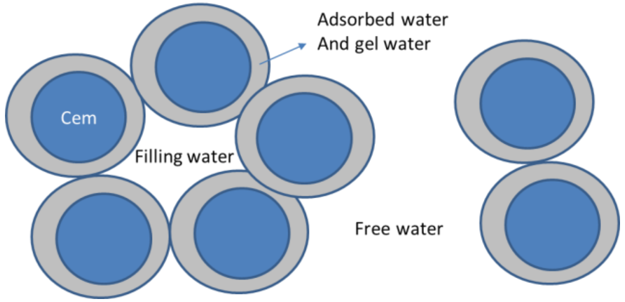
# Mechanisms dominating rheological properties of limestone calcined clay cements

| Sample | *Resting time* | SYS (Pa) | DYS (Pa) | *Thixotropy index* [(SYS-DYS)/DYS] |
|---|---|---|---|---|
| **REF** | 2 min | 27.0 | 21.6 | 0.25 |
| | 60 min | 559.4 | 35.1 | **14.94** |
| **LC3-50** | 2 min | 448.4 | 22.8 | 1.01 |
| | 60 min | 1120 | 274.5 | **3.08** |

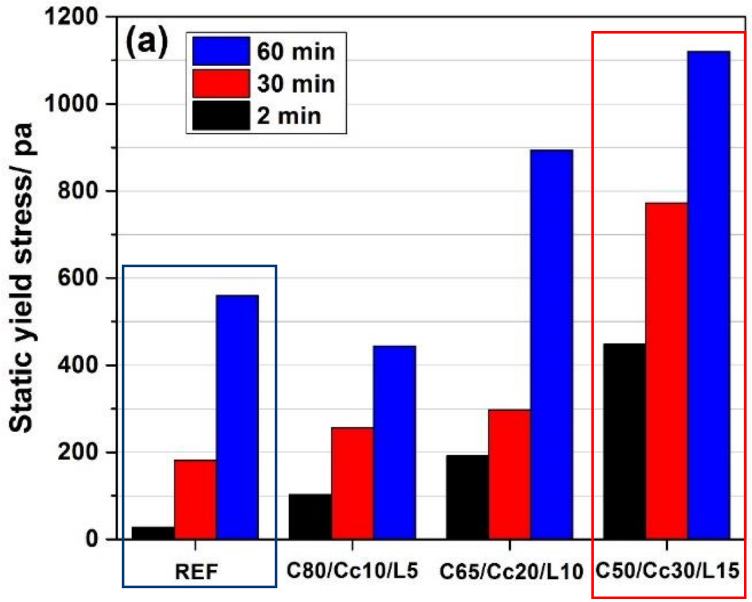


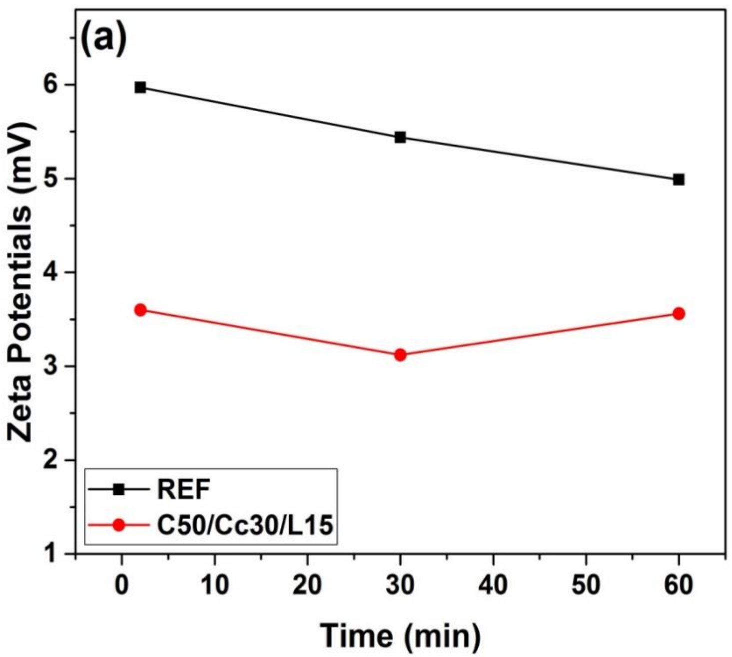

- Comparison at 2 and 60 min shows a significant difference in rate of increase of thixotropy index between LC3-50 REF.
  - **Questions**:
- In OPC:
  - Short term (seconds to mins.) thixotropy: flocculation or colloidal interaction.
  - Long term thixotropy (mins to hours): hydration (CSH nucleation).
- And in limestone calcined clay cement?

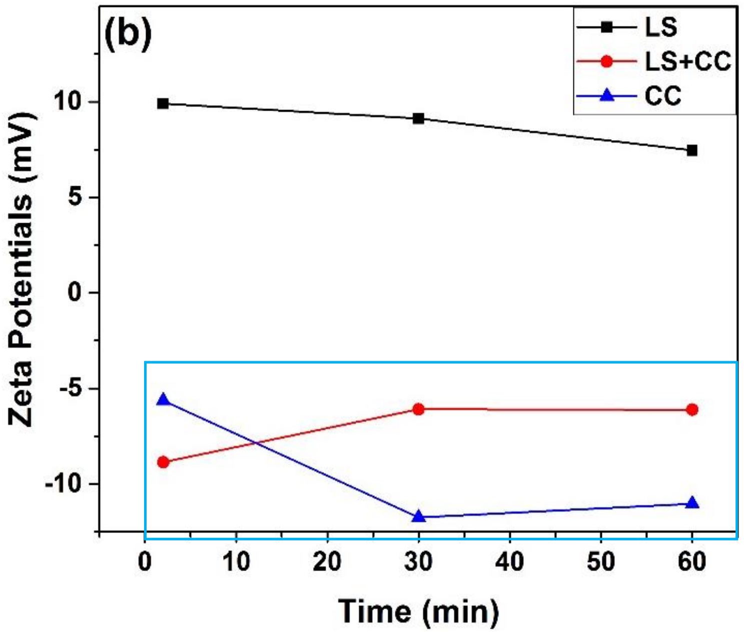
- ✓ Flocculation dominates LC3 systems.
- ✓ Growth in Calcined Clay content => increase in flocculation



# Mechanisms dominating rheological properties of limestone calcined clay cements

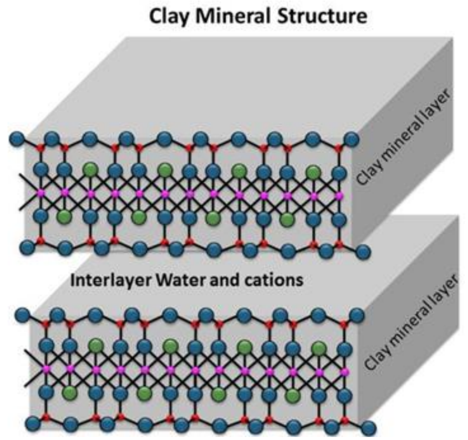


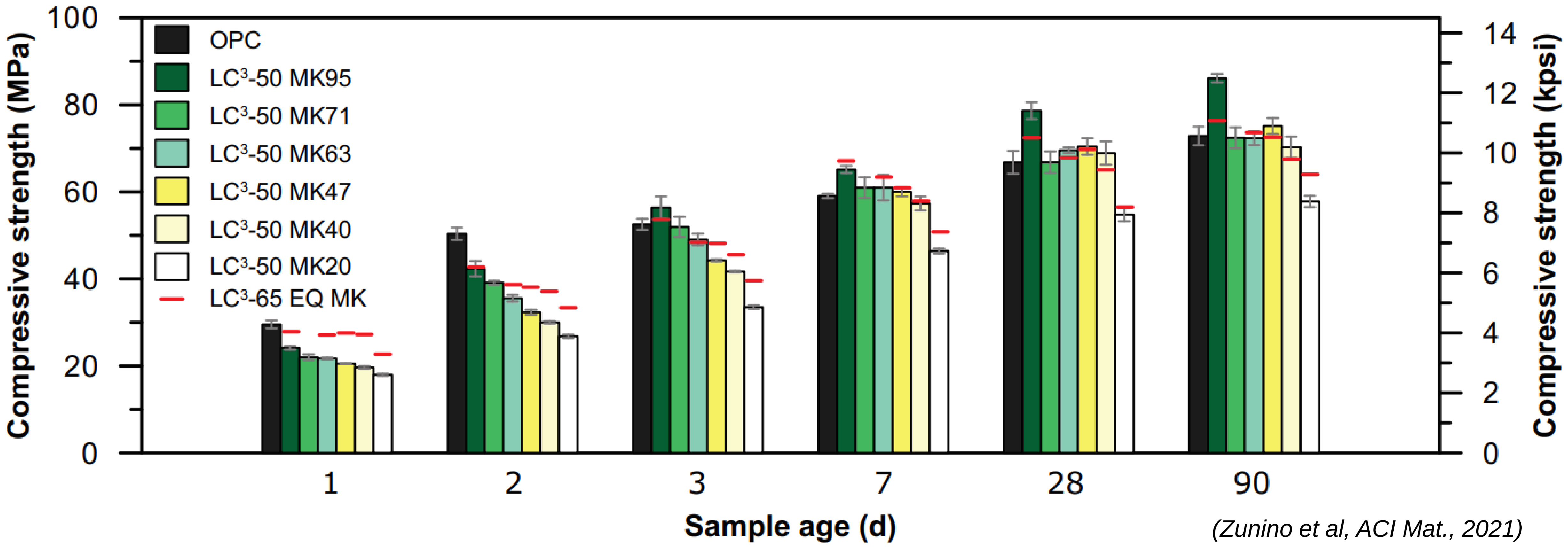




- Thus the origin of the thixotropic buildup of LC3 is not primarily hydration but flocculation.
- Calcined clay dominates LC3 flocculation through the negative surface properties (and platelet morphology + lower density)
- Calcined clay increases the water used as filling water and reduces free layer water, thus reduces flowability.

*(Hou, Muzenda et al, CCR, 2021)*



# Early hydration of limestone calcined clay cements




*(Zunino et al, ACI Mat., 2021)*

- Compressive strength equivalent or greater than OPC can be achieved from 7 d.
- From 1-3 d, strength is lower due to high clinker lower reactivity of metakaolin and the unavailability of CH for pozzolanic reactivity.

# Questions for the current project

1. How do different secondary phases and impurities affect the performance of kaolinitic clays?

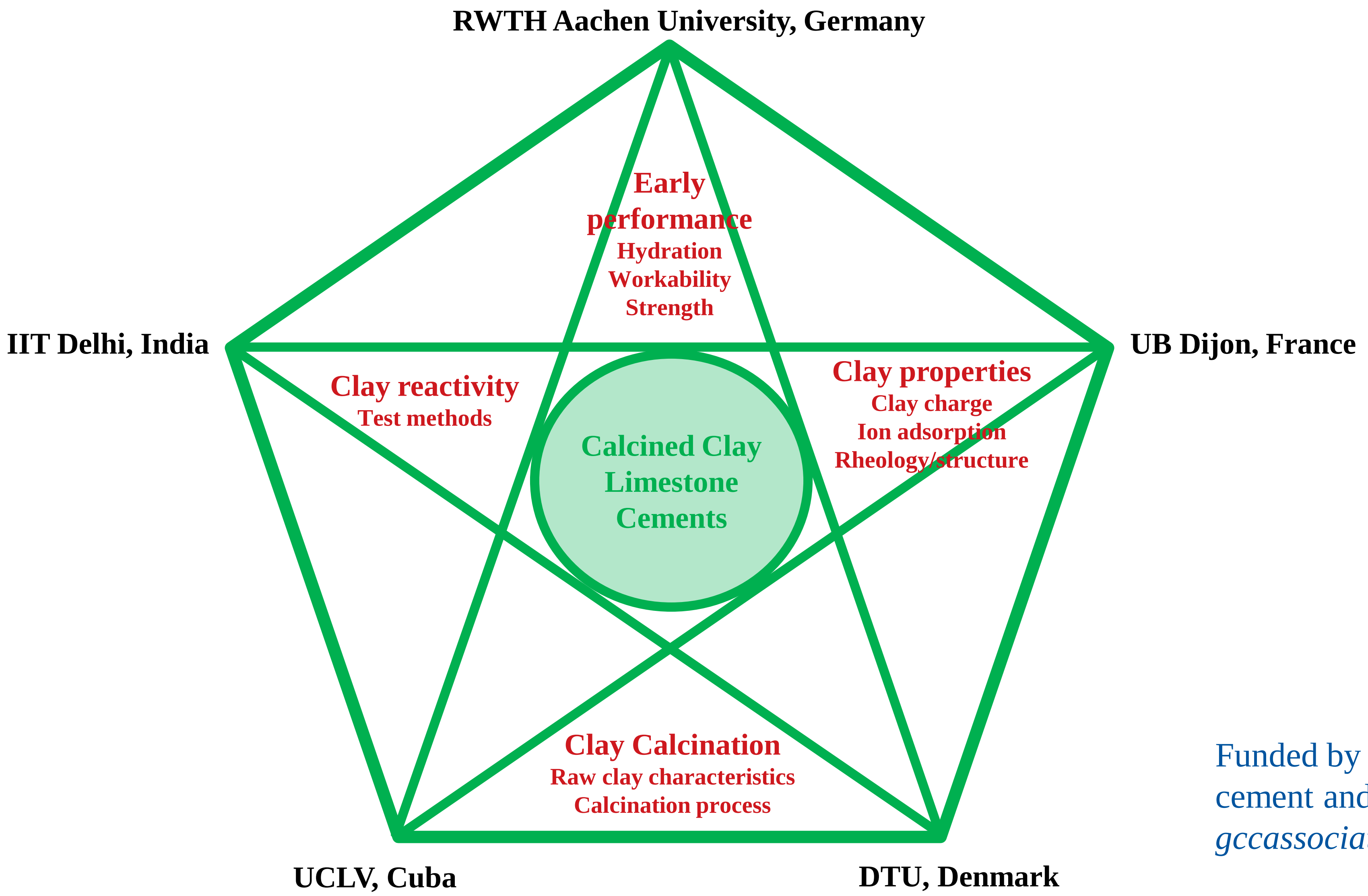
2. What is the influence of clay physiochemical characteristics on the early age hydration of calcined clay limestone cement?

3. How can we better understand the rheology and workability of calcined clay limestone cement and its development for practical applications?

4. How do different clays affect pore solution? How does it evolve after sulfate depletion?

5. What is the relationship between early hydration and setting, microstructure development and strength evolution?

# Ongoing international research project




Funded by Innovandi (global cement and concrete association), *gccassociation.org*.

# Overview of our role and experimental approach

Clay characteristics → Early age hydration

- Pore solution characteristics
- Evolution of rheological properties
- Microstructure development
- Setting and strength evolution

→ Early age hydration model

**Input from partner projects:**

1. Calcination conditions for clays (DTU, Denmark, and UCLV, Cuba)
2. New and rapid methods of characterization of clay reactivity (IIT Delhi, India)
3. Clay physiochemical properties and rheology on pure clay systems (UB Dijon, France)

# Conclusions and outlook

1. Limestone-calcined clay cement has potential to reduce carbon footprint from the cement industry. Its *growing application* leaves us with new challenges to address and new insights to pursue.

2. In terms of rheology, calcined clay increases static and dynamic yield stress, shape stability and cohesive properties. This is due to the physiochemical properties like surface charge and specific surface area.

3. Increased flocculation is the dominating mechanism, which can be addressed through the use of dispersing superplasticizers. An area in which more system-suitable SPs are still needed.

4. At 28 d compressive strength similar to OPC can be obtained but at 1, 3 and 7 d there is a  slow development. Fresh insights in this regard could propel us to fresh solutions.

5. Building a clearer relationship between early hydration and rheology, setting, microstructure development and strength evolution will allow to effectively utilize limestone-calcined clay cement.