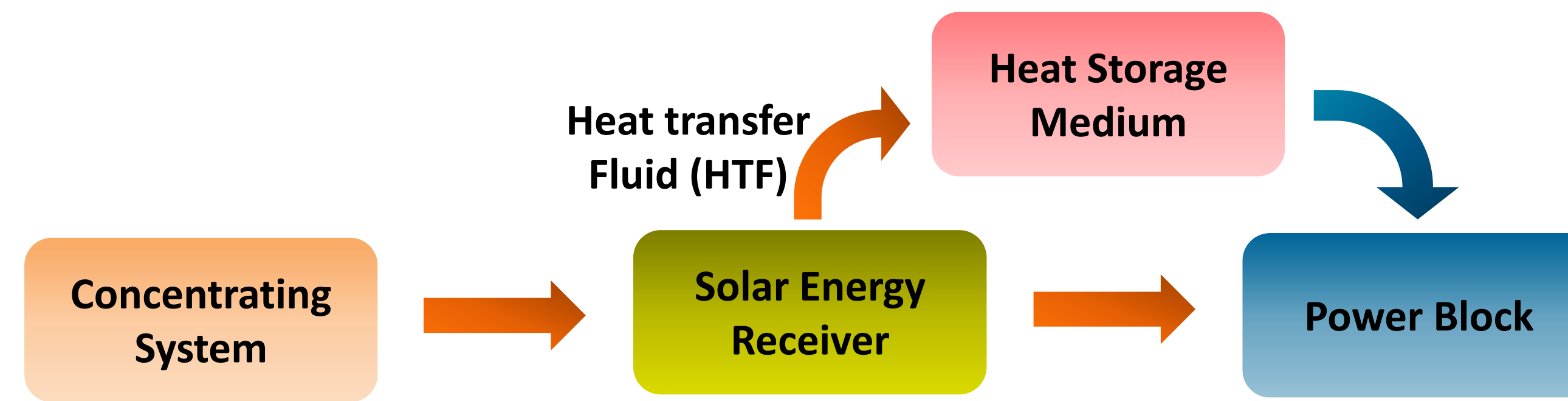


INTRODUCTION

Thermo-Chemical Heat Storage (TCS) is an emerging promising approach in the framework of Thermal Energy Storage (TES) technologies for next generation CSP plants due to its high energy density potential. The current study discusses CaO/Ca(OH)₂ based energy couples and preliminary evaluation of their cyclic hydration/dehydration operation.

On-sun operation – heat storage step



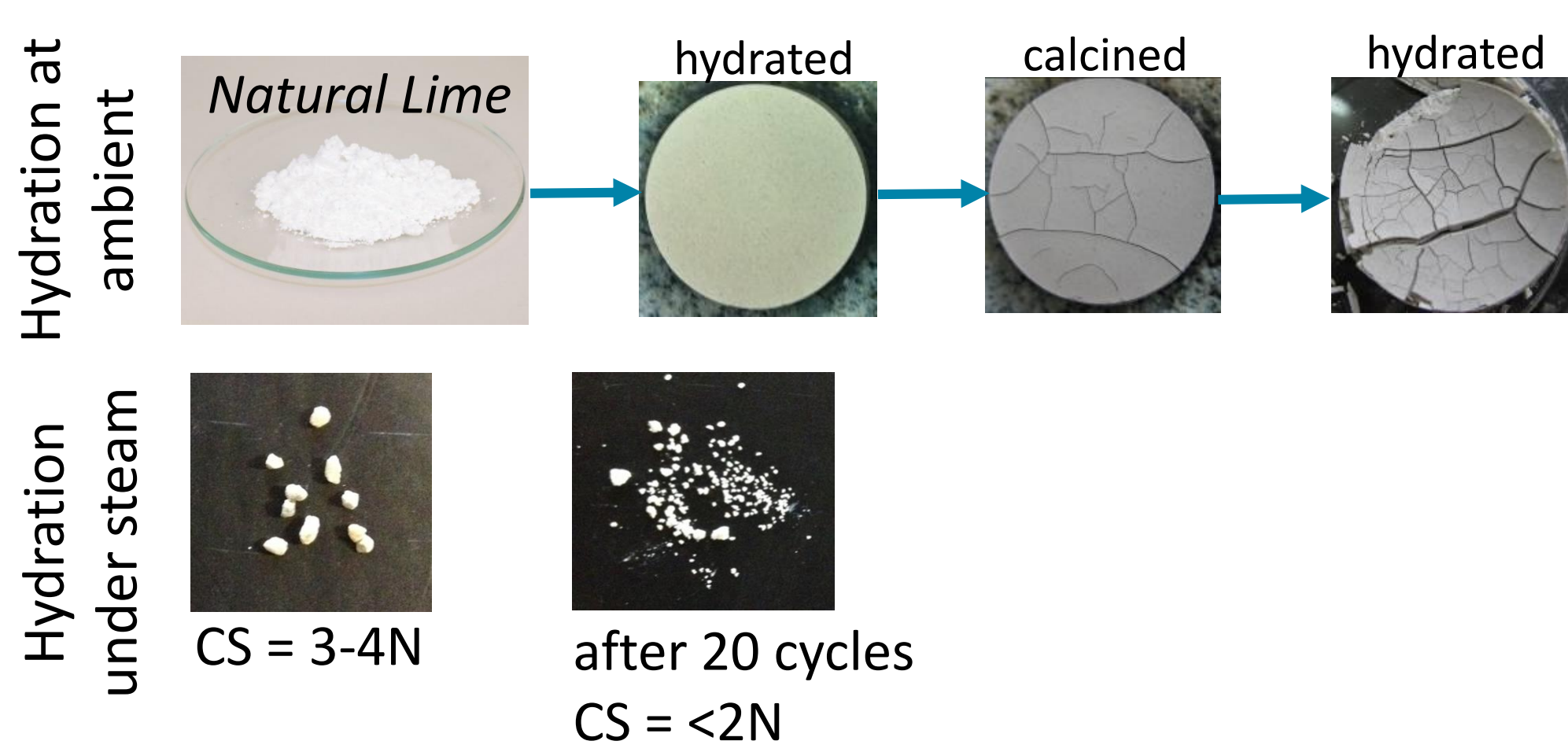
Off-sun operation – heat release step



The main challenge in CaO-based materials relates to severe particles fragmentation with the cycles^[1]. CaO-based composite materials using different binders with cost effective and high temperature resistant materials are developed in order to achieve improved mechanical properties. The present work relates to structural, morphological, mechanical (crushing strength (CS) measurements) & cyclic characterization results.

MAIN CHALLENGE & APPROACH

Particle cycle-to-cycle fragmentation via swelling-shrinkage



APPROACH

CaO-precursors

- ✓ Natural CaCO₃ 1 (≥ 89% wt CaCO₃)
- ✓ Natural CaCO₃ 2 (≥ 99% wt CaCO₃)
- ✓ Commercial CaCO₃ powder

Structural stabilizing agents (binders)

- ✓ Fumed nanosilica (SiO₂)
- ✓ Kaolinitic Clay^[2, 3]
- ✓ Sodium silicate solution (Na₂Si₃O₇)^[4]

Key parameters

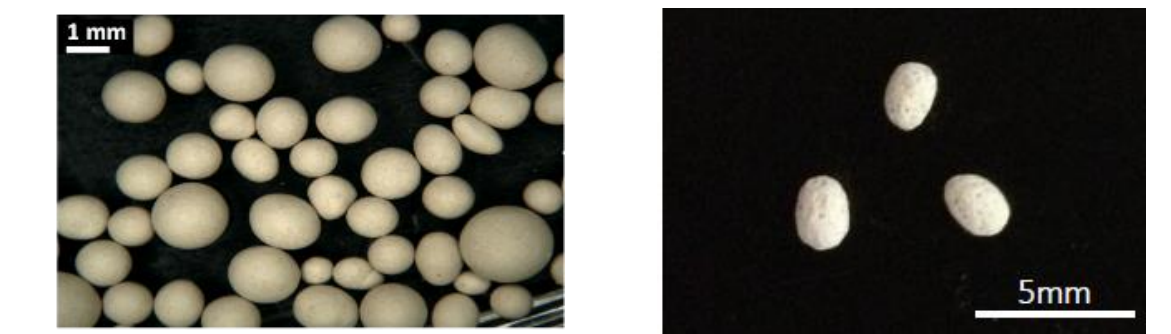
- ✓ CaCO₃ particle size
- ✓ CaO/binder ratio: 10-25% wt
- ✓ Stabilization conditions

Stabilization via thermal treatment

- ✓ SiO₂ & clay composite formulations: calcination in air at temperatures 750-900°C
- ✓ Sodium silicate composites: 2-step procedure with final calcination in air up to 850°C and/or CO₂ treatment above 750°C.

Manufacturing of composite formulations

- ✓ Solid mechanical mixing of powder precursors
- ✓ Water added as a binder
- ✓ Green small structured bodies



STRUCTURAL, MORPHOLOGICAL & MECHANICAL PROPERTIES

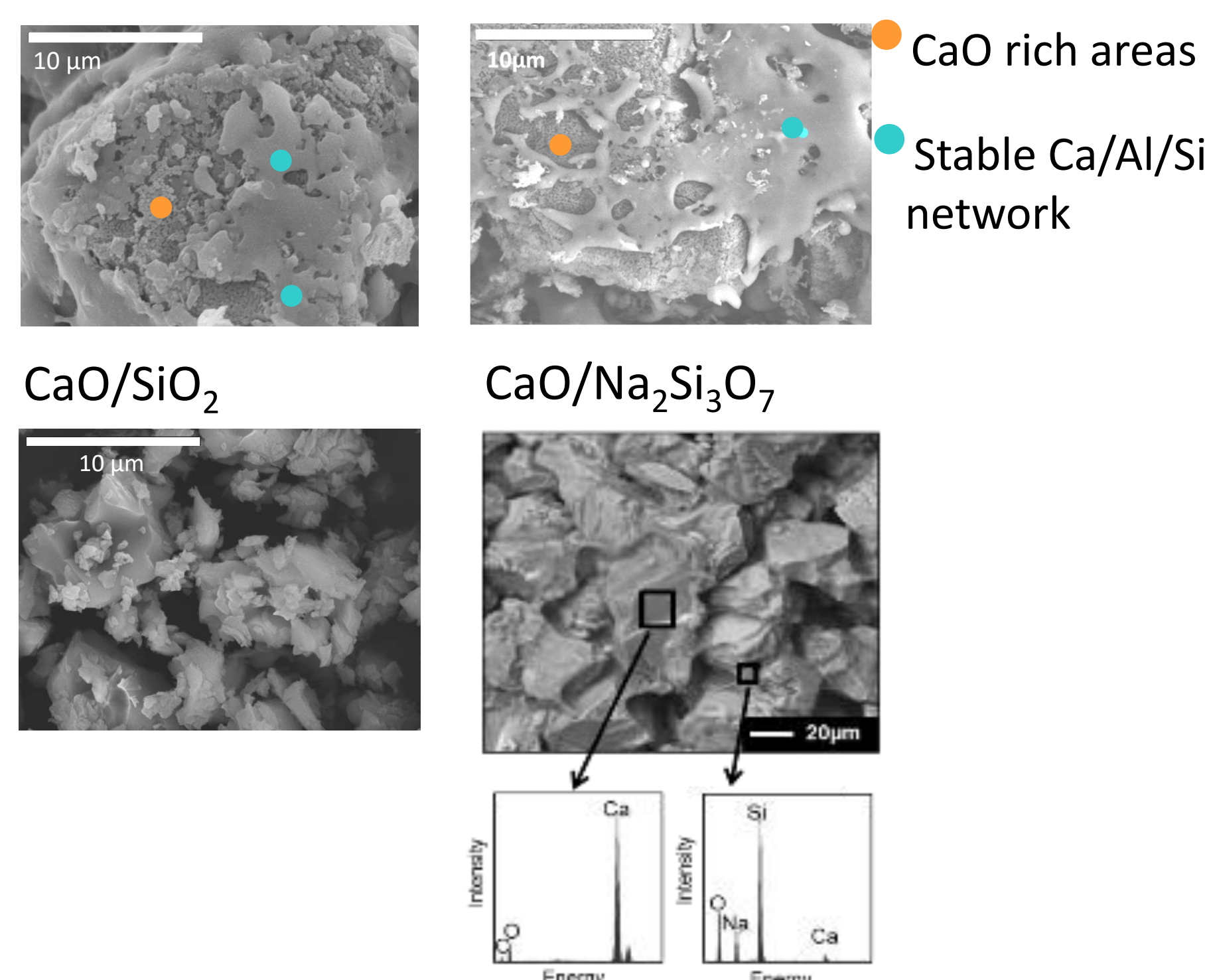
Composition identified by X-Ray Diffraction

Mechanical strength by CS measurements

Material	T _{calcination} °C	Composition	CS _{fresh} N
Natural CaCO ₃ 1 & 2	-	CaCO ₃	7-9
Natural CaCO ₃ 2	900	CaO, traces of Ca(OH) ₂	0.2
Natural CaCO ₃ 1	750	CaO, CaCO ₃	17
Natural1/clay=90/10	900	CaO, Ca ₂ Al ₂ SiO ₇ , SiO ₂	6
Natural1/clay=90/10	750	CaO, CaCO ₃ , SiO ₂	2
Natural1/clay=75/25	900	CaO, Ca₂Al₂SiO₇, SiO₂	19
Natural1/clay=75/25	750	CaO, CaCO ₃ , SiO ₂	5
Natural2/clay=75/25	900	CaO, Ca₂Al₂SiO₇, SiO₂	30
Natural1/SiO ₂ =90/10	900	CaO, Ca ₂ SiO ₄	n/a
Natural1/SiO ₂ =80/20	900	CaO, Ca ₂ SiO ₄	n/a
Natural2/Na₂Si₃O₇=85/15	850	CaO, Ca₂SiO₄, Na₂CaSiO₄, SiO₂	18
Natural2/Na ₂ Si ₃ O ₇ =90/10	850	CaO, Ca ₂ SiO ₄ , Na ₂ CaSiO ₄ , SiO ₂	5
Natural2/Na ₂ Si ₃ O ₇ =75/25	850	CaO, Ca ₂ SiO ₄ , Na ₂ CaSiO ₄ , SiO ₂	20

Morphological characterization via SEM:

CaO/clay composite



CaO/SiO₂ composites: Low structural stability

CaO/clay composites:

- **Low calcination temperatures:** no mixed phases formation → **poor structural stability** (low CS)
- **Mixed Ca/Al/Si** phases formation at high calcination temperatures. **Solid network** (Ca/Al/Si oxide) for 25wt% clay content → **enhanced structural integrity (CS>19N)**
- ✓ **CaO/Na₂Si₃O₇ composites:** Mixed CaO and sodium silicate phases formation leading to enhanced structural stability
- ✓ **Mixed oxides formed at the expense of free CaO**

MULTI-CYCLIC HYDRATION/DEHYDRATION EVALUATION

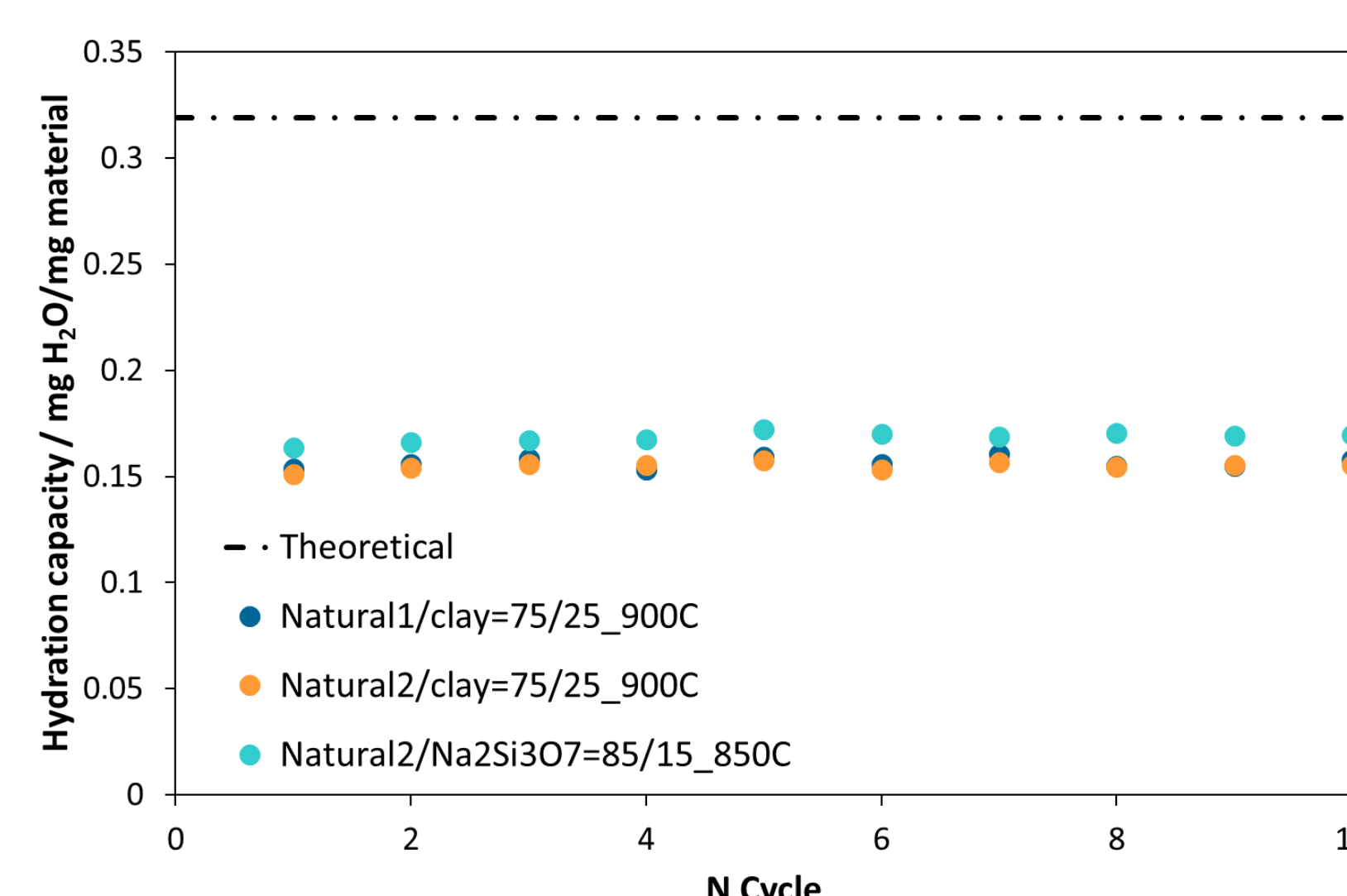
Hydration-dehydration in a TGA setup^[5]

- ✓ Up to 10 cycles
- ✓ Hydration at 450°C under pure steam (20g/h)
- ✓ Dehydration at 500°C under air (26.2Ln/h) and at 550°C under pure steam (20g/h).

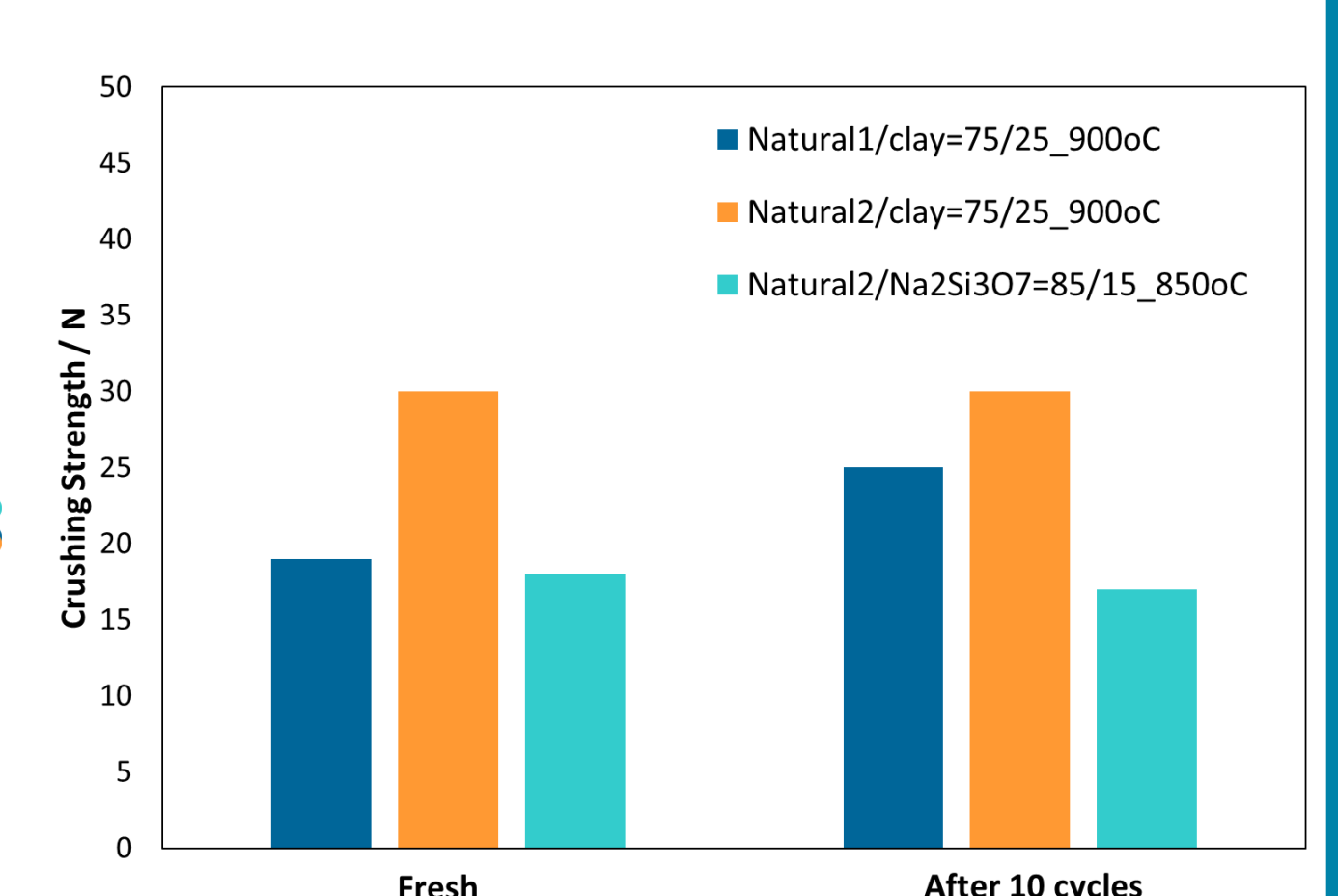
Material	Hydration capacity		Hydration efficiency		CS _{after 10 cycles} N
	mg H ₂ O / mg material	mg H ₂ O / mg material	% theoretical value*	% theoretical value*	
Natural CaCO ₃ 2	0.315	0.315	99	99	0
Natural1/clay=90/10_900°C	0.215	0.217	67	68	0.2
Natural1/clay=90/10_750°C	0.185	0.149	58	47	0.1
Natural1/clay=75/25_900°C	0.157	0.158	49	50	25
Natural1/clay=75/25_750°C	0.187	0.106	59	33	0.4
Natural2/clay=75/25_900°C	0.168	0.155	53	49	30
Natural1/SiO ₂ =90/10_900°C	0.096	n/a	30	n/a	0
Natural2/Na₂Si₃O₇=85/15_850°C	0.170	0.169	54	53	17
Natural 2/Na ₂ Si ₃ O ₇ =90/10_850°C	n/a	0.229	n/a	72	1
Natural 2/Na ₂ Si ₃ O ₇ =75/25_850°C	n/a	0.112	n/a	35	18

* Efficiency w.r.t. theoretical value 0.319 mg H₂O/mg CaO

Hydration/dehydration performance



Mechanical properties evaluation



- ✓ **Promising combination of stable hydration performance and mechanical stability**
- ✓ Additive content and calcination temperature → critical parameters
- ✓ Clay & sodium silicate composites with high additive content preserved their mechanical stability with cycles. **High CS values (>15N)** were assigned to Ca/Al/Si & Ca/Na/Si phases.
- ✓ **Stable hydration performance** of around 50% of theoretical in the course of 10 cycles

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