# Thermodynamic and Kinetic Analysis of Cementitious Reactions in Lime-treated Clays

Tasneem Ahmadullah and Maria Chrysochoou
Department of Civil and Environmental Engineering
University of Connecticut

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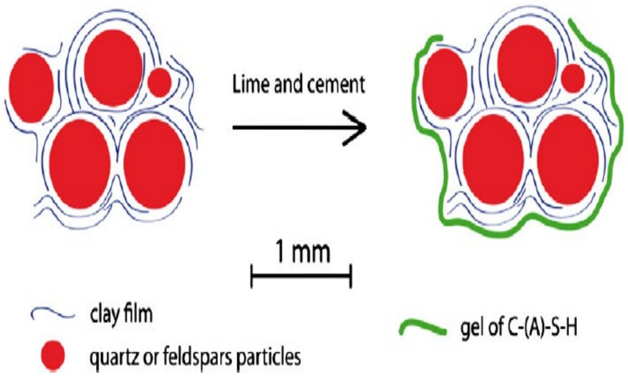
UCONN

# Background and Motivation

Surface view of a near vertical Bentonite layer. The layer heaved with a differential displacement of 3 inches within 24 hours after a rainstorm at this construction site (Source: Colorado Geological Survey))

- Damage caused by clay swelling in subgrade costs $1 billion every year in the US alone
- Most common treatment method is addition of lime and cement or cementitious materials.
- The mix design is done mostly empirically using short term (28-day) strength tests.

# Clay stabilization mechanisms – *qualitative understanding*




Lime or cement forms a gel of silica hydrate which gives clay structure strength (source: Kavak & Baykal 2012)

**Solid (Clay Mineral) + Water + Stabilizer (CaO)**

↓

**Solution**

↓

**Solid (CAH/CSH)**

**E.g. $Al_2Si_2O_5(OH)_{2(s)}$ (Kaolinite) + $CaO_{(s)}$**

↓

**$Al^{3+}_{(aq)} + H_4SiO_4^{0}{}_{(aq)}$**

↓

**$Ca_5Si_6O_{16}(OH)_2.4H_2O_{(s)}$ (CSH)**
**+**
**$Ca_4Al_2O_7.13H_2O_{(s)}$ (CAH)**

↑ **Strength**
↓ **Swelling**

# Clay stabilization mechanisms – *quantitative understanding*

## Chrysochoou (2014)
## Kaolinite XRD and UCS

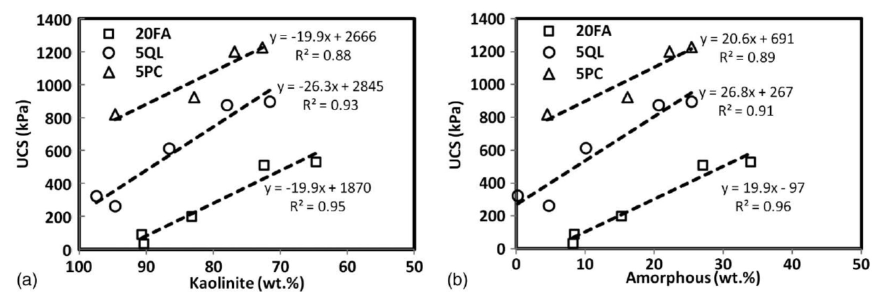



**Fig. 6.** Correlation between average UCS and (a) kaolinite content and average UCS; (b) amorphous content

## Maubec et al. (2017)
## Kaolinite and Ca-bentonite TGA and UCS

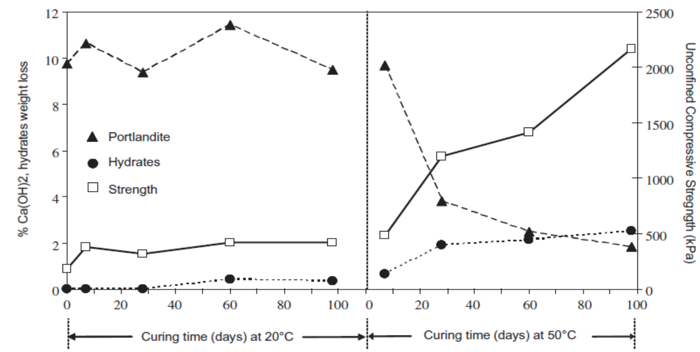



**Fig. 8.** Evolution of portlandite, hydrates weight losses and unconfined compressive strength with time at 20 °C and 50 °C for the kaolinitic material treated with 10% of lime.

## De Windt et al. (2014) Ca-bentonite Modeling and NMR, TGA, XRD

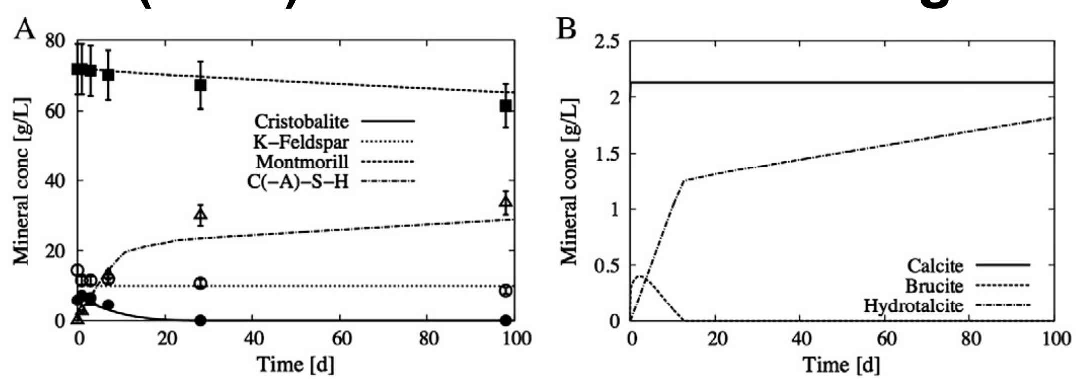



**Fig. 1.** Evolution with time of the primary phases of bentonite and the pozzolanic phases obtained by modeling and $^{29}$Si NMR analysis at 20 °C; symbols correspond to experimental data (square ■ = montmorillonite, triangle △ = C(−A)–S–H, empty circle ○ = K-feldspars and solid circle ● = cristobalite).

# Objectives

**Replicate and expand scope of study**

- Kaolinite + 5% lime
- Na-bentonite + 8% lime
- Study up to 720 days of curing

**Method adoption and refinement**

- Extract and analyze pore water solution
- Use NMR, XRD, TGA

**Model development**

- Comparison with Ca-bentonite

# Clay mineral properties

| Clay | Na-Bentonite | K90 |
|---|---|---|
| Source | Performance Minerals | KaMin LLC |
| Liquid Limit | 384 | 37 |
| Plastic Limit | 68 | 24 |
| Percent <2 µm | 75 | 85 |
| Percent <10 µm | 85 | 100 |
| Percent <75 µm | 90 | 100 |
| Mineralogy | Na-montmorillonite (~80%), Na-clinoptilolite, quartz, cristobalite, anorthite, muscovite | kaolinite |

# Methodology

Preparation of compacted monolith

→ Breakdown of sample by UCS after curing time completion

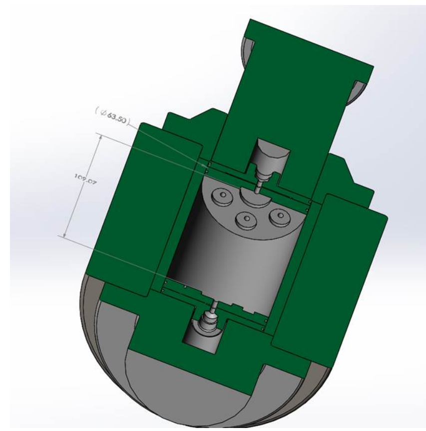
→ Extraction of pore water by applying static load on broken sample → Elemental Analysis ( Na K, Ca, Mg, Fe, Si, Al & C)

→ Drying of solid using IPA and acetone → Spectroscopic analysis

(XRD, TGA, NMR)

# Pore water extraction

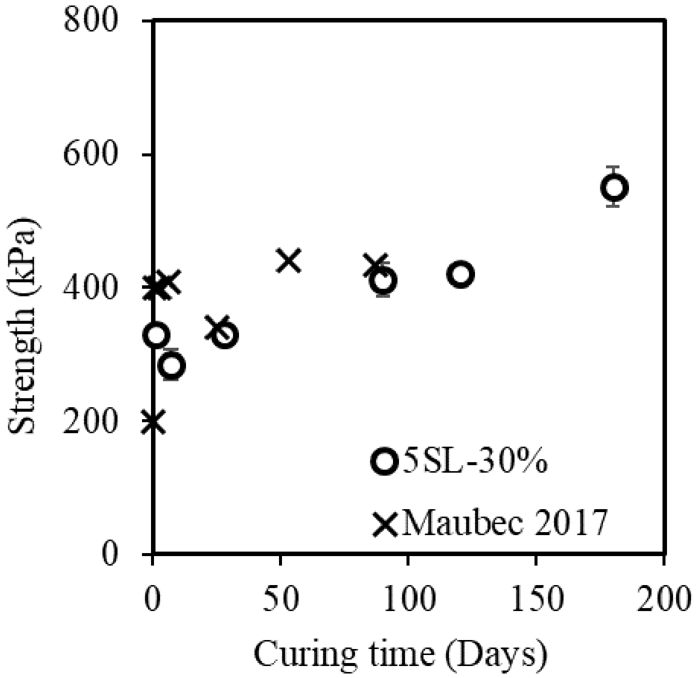
Custom-made pore water extraction device for clay



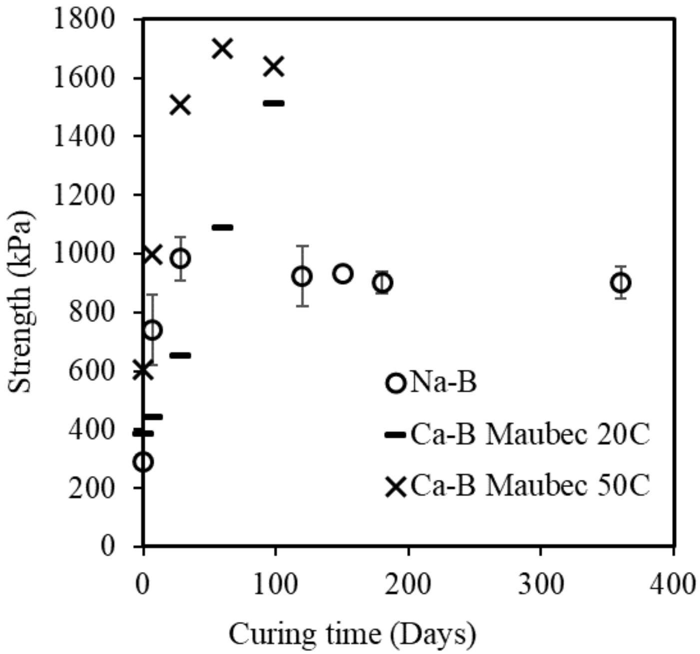
| Squeezed Material | Extraction Pressure (MPa) | Extraction Duration (h) | Moisture content (%) | Extraction Efficiency (%) |
|---|---|---|---|---|
| B-8SL | 690-1379 | 5 | 40 | 4.2 |
| K90-5SL | 690-1000 | 2 | 30 | 56 |

# UCS results

## Kaolinite + 5% Lime

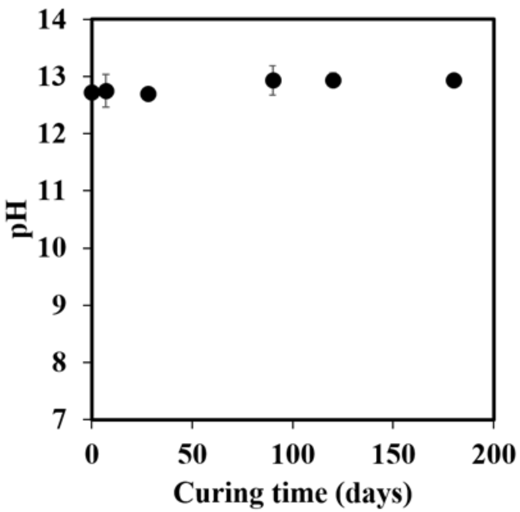



## Na-bentonite + 8% Lime

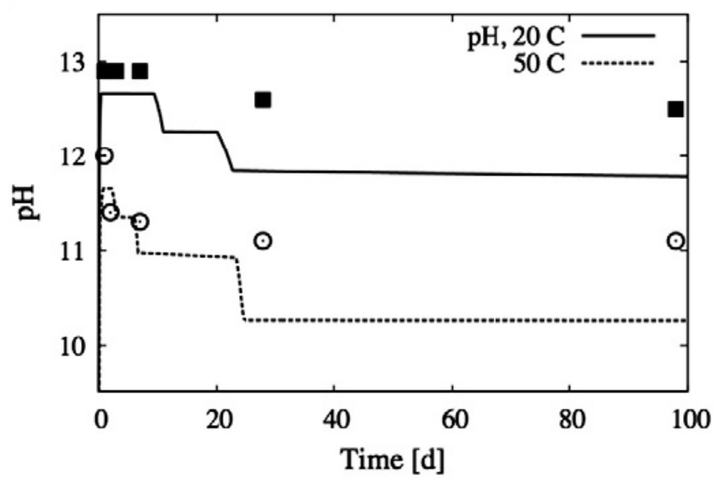


# Solution results - pH

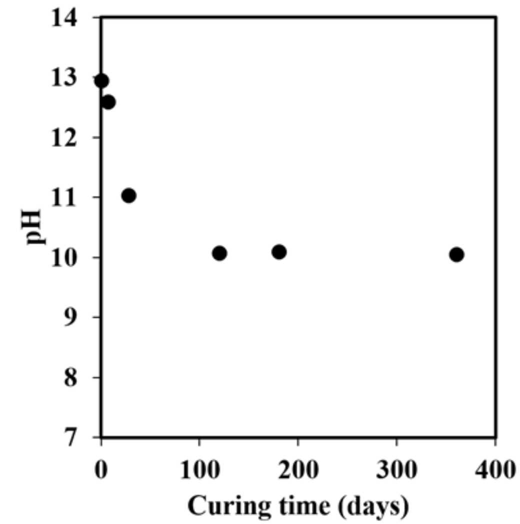
**Kaolinite**




**Ca-bentonite + 10% Lime, DeWindt 2014**

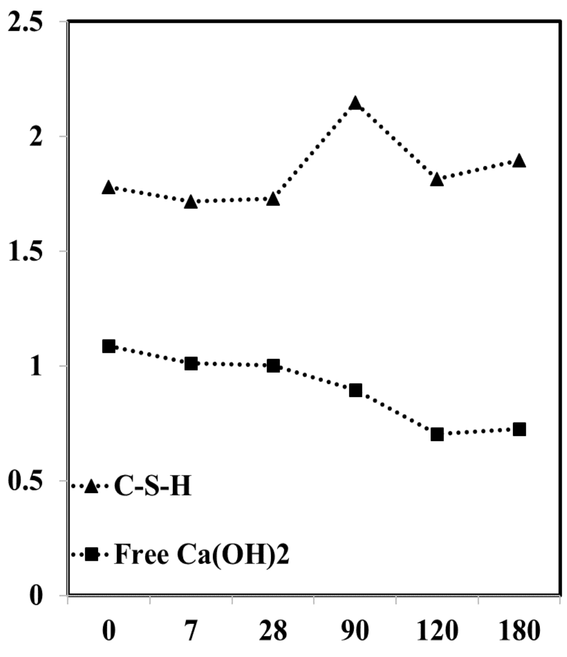



**Na-bentonite**

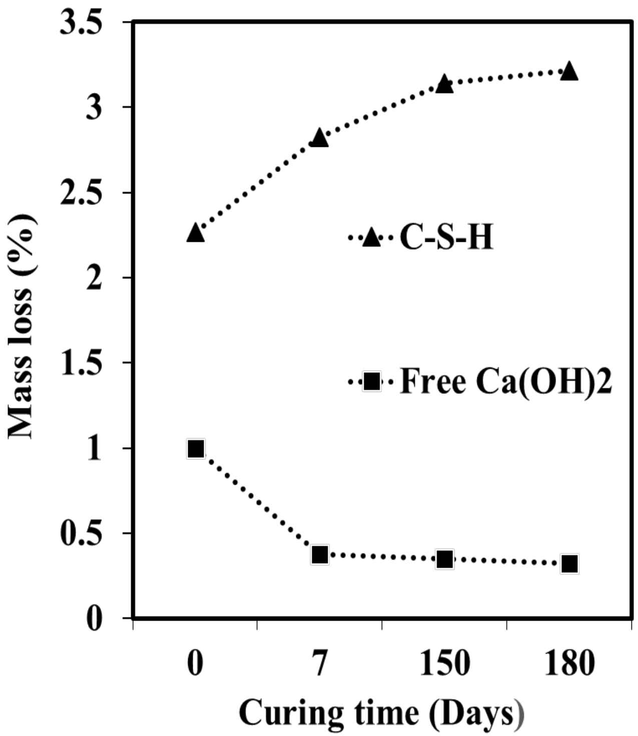


# TGA Analysis

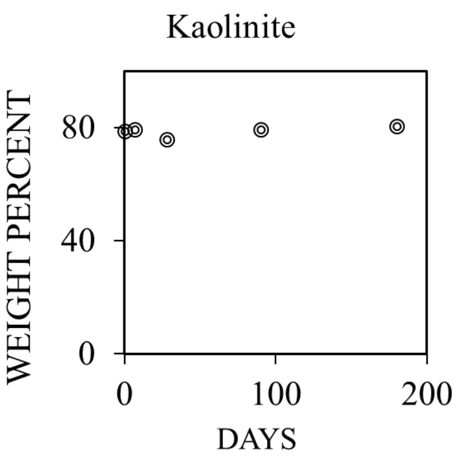
**Kaolinite**



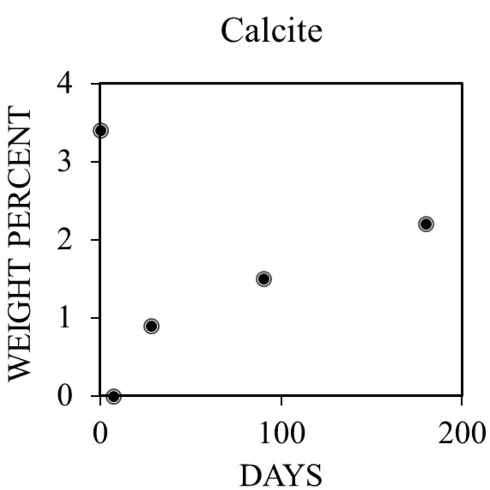

**Na-Bentonite**

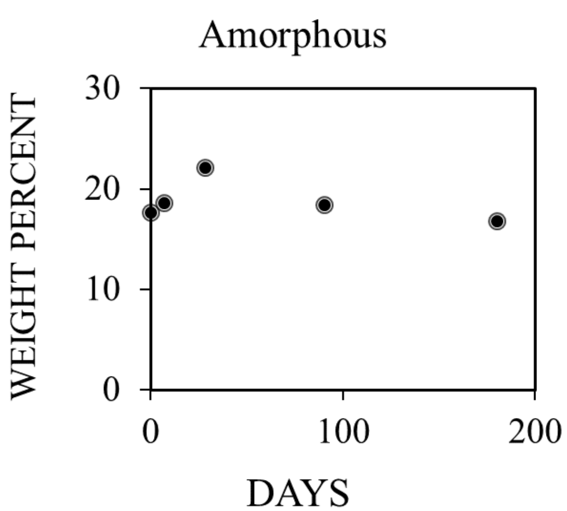


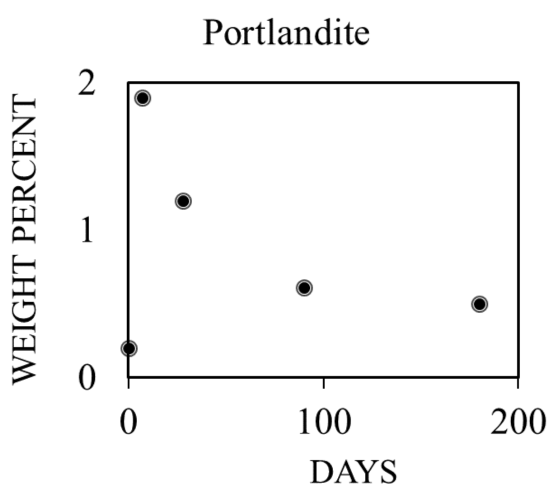
# XRD Analysis (Kaolinite)




- The XRD analyses were done using 20% corundum ($Al_2O_3$) as internal standard.
- The maximum decomposition of kaolinite was 5%
- Portlandite ($Ca(OH)_2$) progressively turns into calcite $CaCO_3$ as a result of carbonation.



# Conclusions

**Kaolinite**

- Data collected so far agrees with kaolinite literature data.
- Kaolinite has not reached equilibrium within the shown 180 days, needs further study.
- Spectroscopic data indicates that carbonation of hydrated lime is the primary reaction, with little evidence for substantial CSH formation. This correlates with limited strength gain over time.

**Na-Bentonite**

- Na-Bentonite reacts and gains strength faster than kaolinite reaching a plateau by 120 days.
- Compared to literature, this behavior is different than Ca-bentonite, which shows continued reaction up to 90 days.
- Lime consumption is fast, decreasing the pH in the same time frame and forming hydration products (CSH) as confirmed by spectroscopy.