THE USE OF IMPURE CLAYS AS SUPPLEMENTARY CEMENTITIOUS MATERIALS

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Calcined Clays

- Metakaolin is a commercially available supplementary cementitious material
- But pure kaolinite is expensive and has other high-end uses

Metakaolin

High Reactivity Metakaolin
The White Alternative to Silica Fume

Manufactured For:

- High Strength & High Performance Concrete
- Grouts, Mortars, Blended Cement Products
- Architectural Precast & Decorative Concrete
- Stone / Brick Veneer & GFRC

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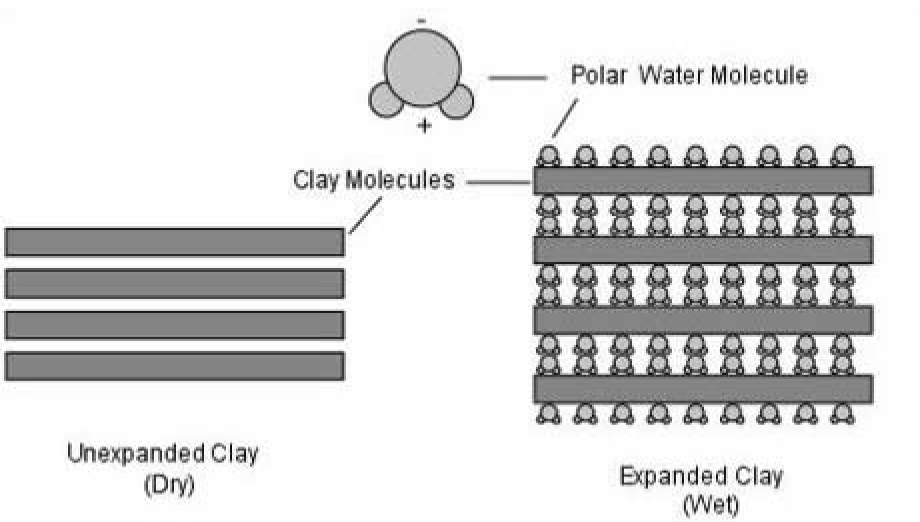
Other clay minerals

- Most “real” or “impure” clays are combinations of:
  - Clay minerals such as:
    - Kaolinite
    - Illite
    - Montmorillonite/smectite
    - Palygorskite
  - And crystalline phases like:
    - Quartz
    - Calcite
    - Feldspars
    - Anatase
  - $SiO_2+Al_2O_3+Fe_2O_3 > 70\%$

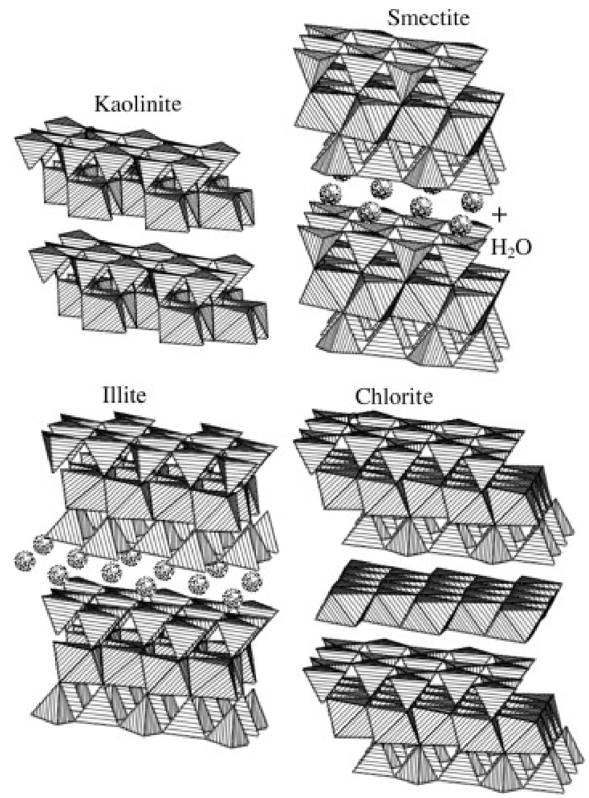
Challenges with impure clays as SCMs

1. Increased water demand
   - High specific surface area of materials
   - Expansive clay minerals



geology.ar.gov

2. Low pozzolanicity
   - High crystallinity



Allard et al., Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, Volume 277, 15 April 2012, Pages 112–120.

Important factors affecting clay performance

- Water demand related to:
  - Surface area (BET)
  - Calcination

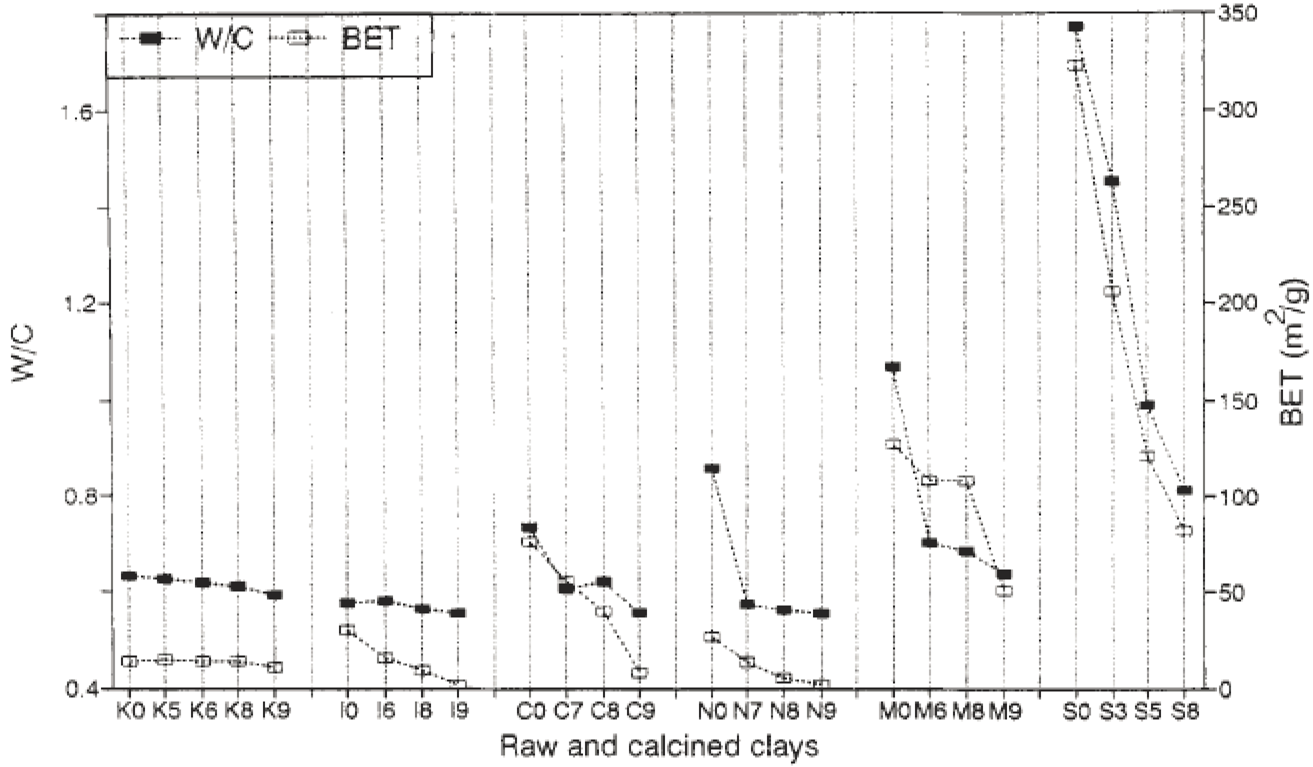


FIG. 1.

W/C: Water/(cement+clay) ratio of the mortars (flow=100%), and BET specific surface area of the used clays (nitrogen absorption). Connection lines between data points do not have physical meaning.

Abbreviations in all the Figs: K=kaolinite, I=illite, C=Ca-montmorillonite, N=Na-montmorillonite, M=mixed layer mica/smectite and S=sepiolite. Numbers beside these letters indicate the calcination temperature rounded down to the nearest hundred degrees (°C), e.g. K5=kaolin calcined above 500°C. 0 indicates clay without calcination.

He et al. Cem. Con. Res. 1995.

Important factors affecting clay performance

- Reactivity
  - Calcination temperature: Crystallinity/degree of dehydroxylation
  - Clay mineral type

- He et al. (Cem Conc Res 1995) determined optimal calcination temperatures:
  - Ca/Na-montmorillonite 830°C, kaolinite 650°C, and mixed layer clay 960°C
  - All increased the compressive strength over neat cement mortars at 28 days cured at 40C.
- Habert et al. (Appl Clay Sci 2009) listed optimal calcination temperatures as:
  - Montmorillonite 800°C, kaolinte 700 °C for kaolinite, palygorskite 750°C , illite 850°C
  - Stressed that while dehydroxylation is desired, re-crystallization should be avoided
  - Clay mineral doesn't matter nearly as much as degree of crystallinity

- Tironi et al. (Const Build Mat 2012): more disordered the kaolinite structure prior to calcination, the greater the pozzolanic reactivity

- He et al. (Appl Clay Sci 2000): calcined sepiolite and illite less reactive
  - Confirmed by Fernandez et al. (Cem Conc Res 2011) for illite

Filler effect

R. Fernandez et al. / Cement and Concrete Research 41 (2011) 113–122

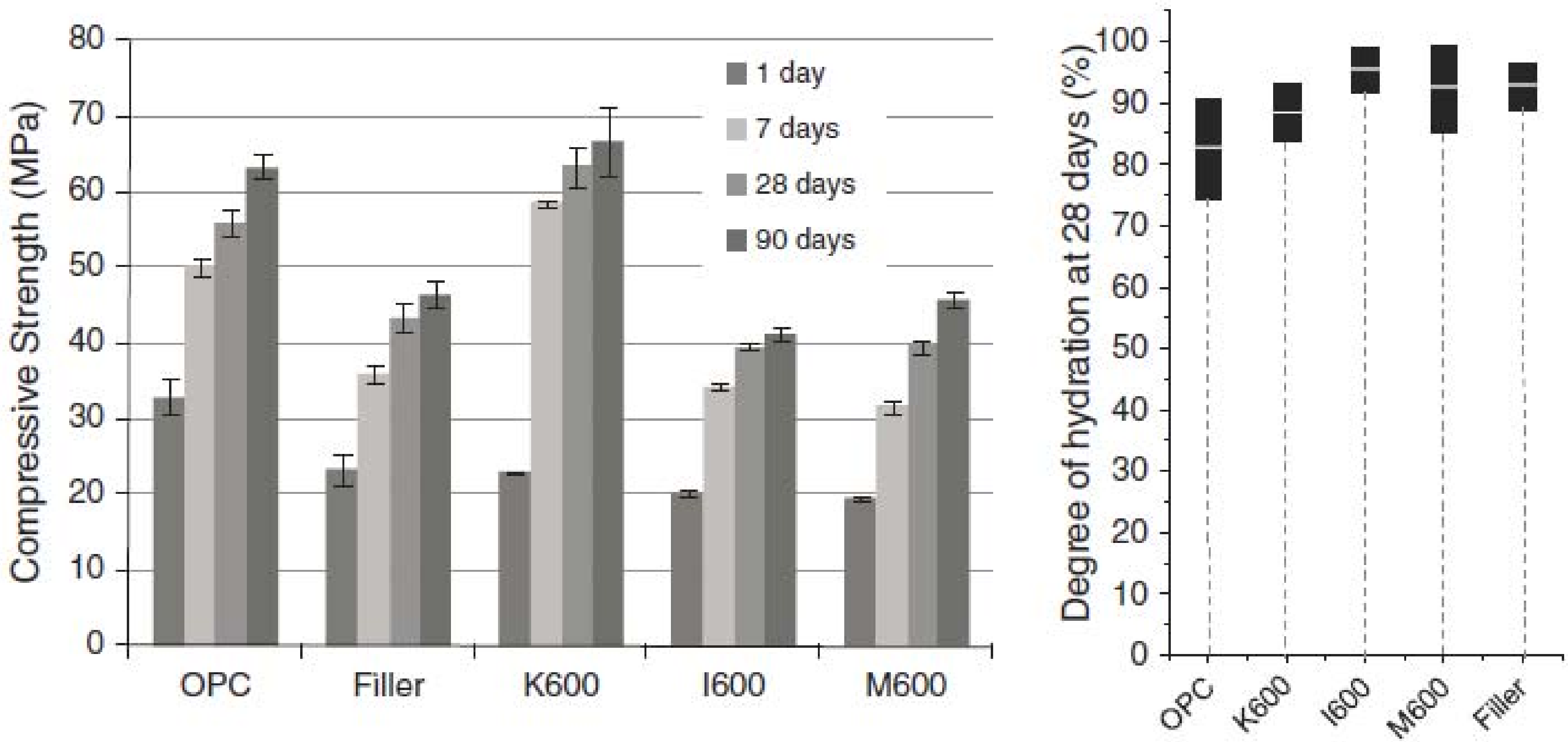


Fig. 13. Compressive strength and degree of hydration at 28 days of calcined-clay-cement mortars.

Increasing the reactivity of calcined clays

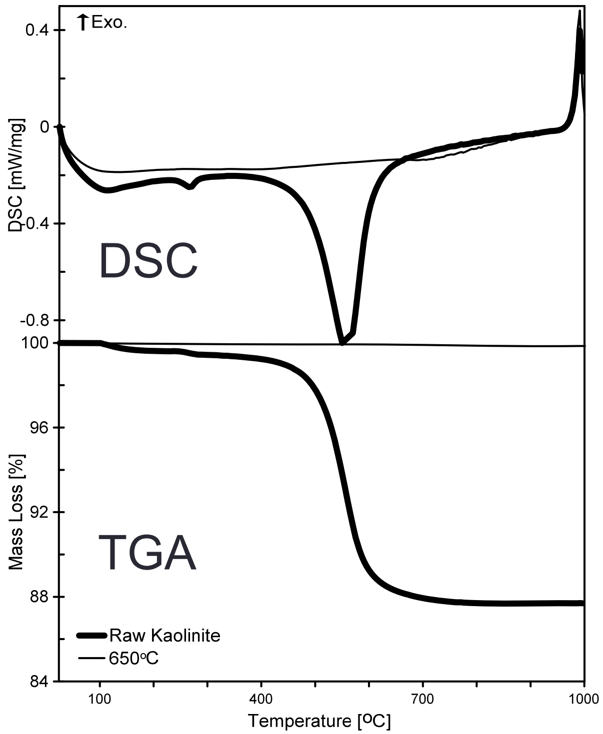
- Acid treatment: 6 M HCl resulted in a high surface area amorphous silica in metakaolin (Belver et al., 2002)

- Iron Oxide: Lowered the refractoriness (i.e. thermal resistance) of calcined kaolinite (Kuechler,1926)

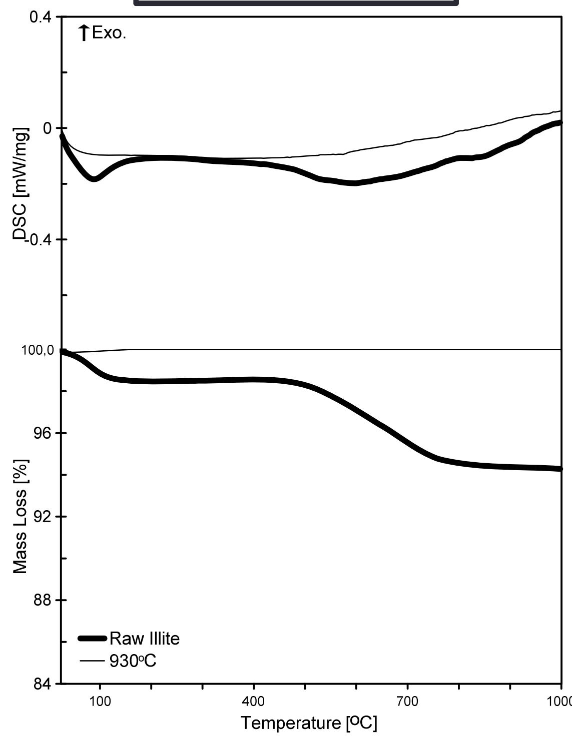
- Iron Oxide: Increased the pozzolanic activity of *surkhi* (a finely powdered burnt clay) (Srinivasan,1956)

- Zinc Oxide: Changed reactivity of kaolinite measured by lime reactivity tests (Chatterji et al.,1960)

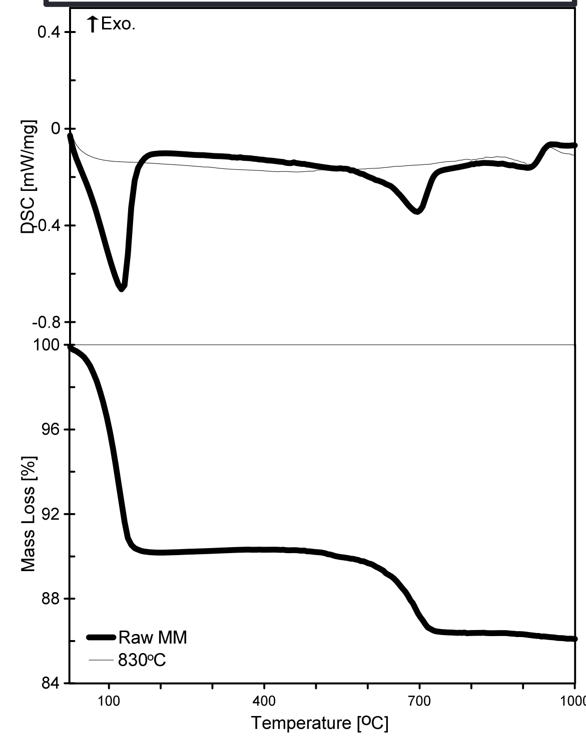
Kaolinite 650°C

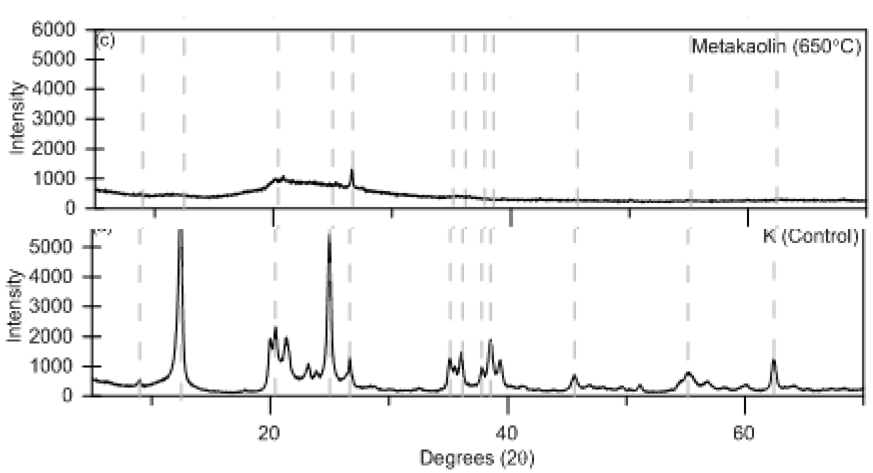


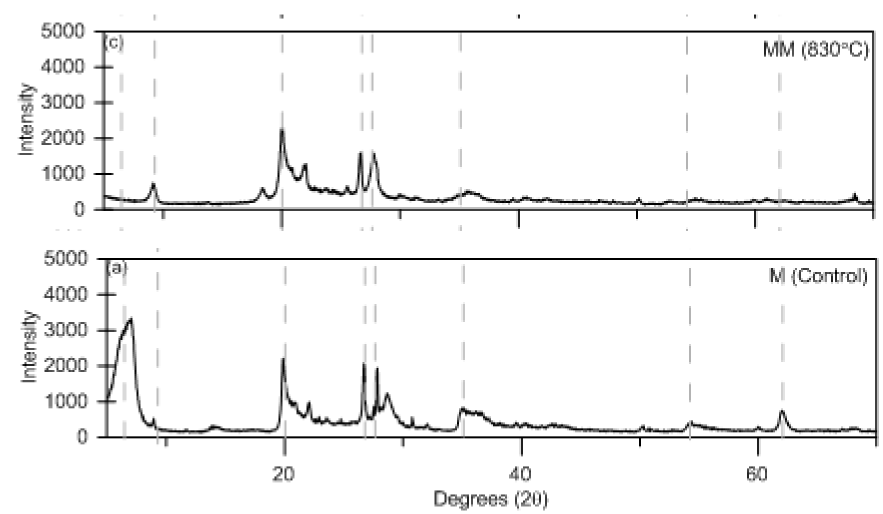
Illite 930°C



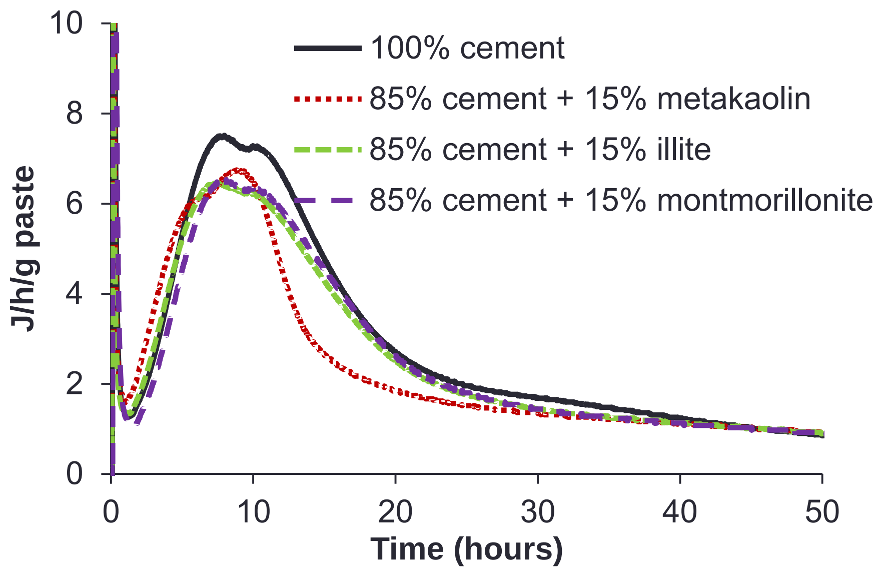
Montmorillonite 800°C

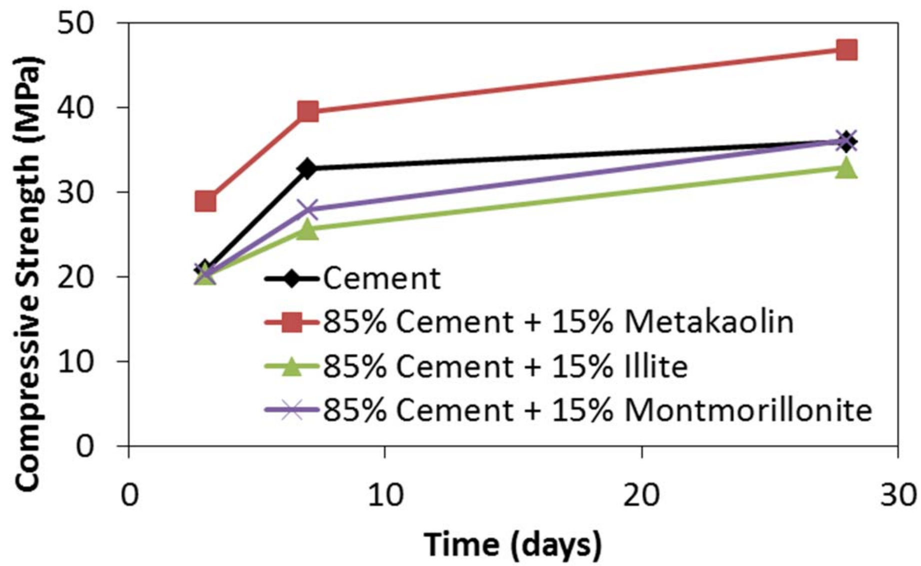




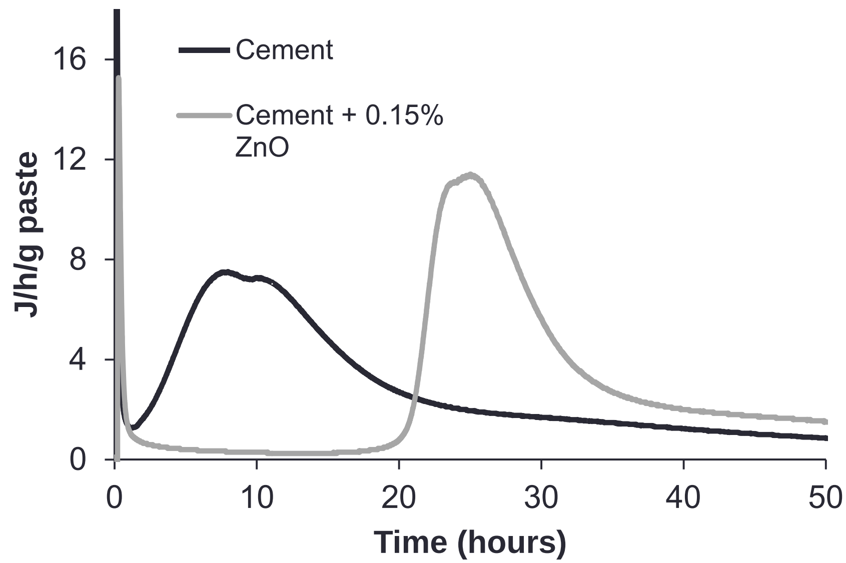


Reactivity of Calcined Model Clays



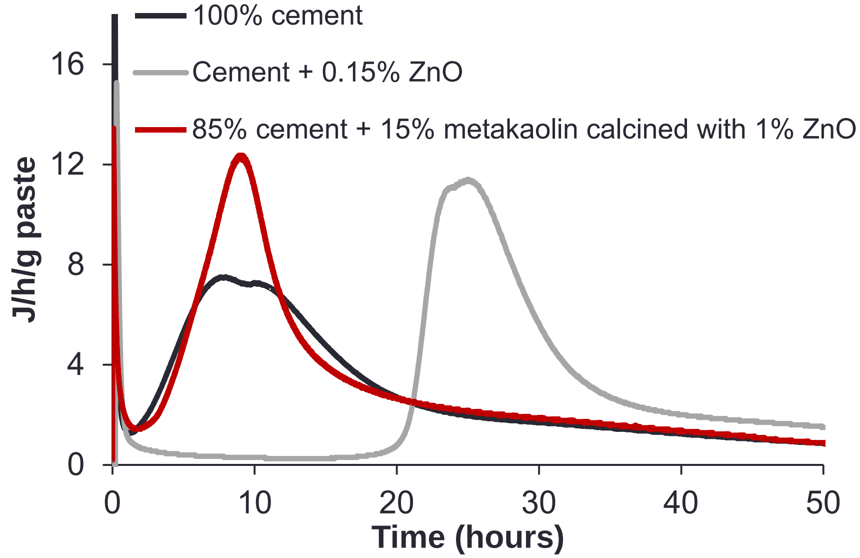


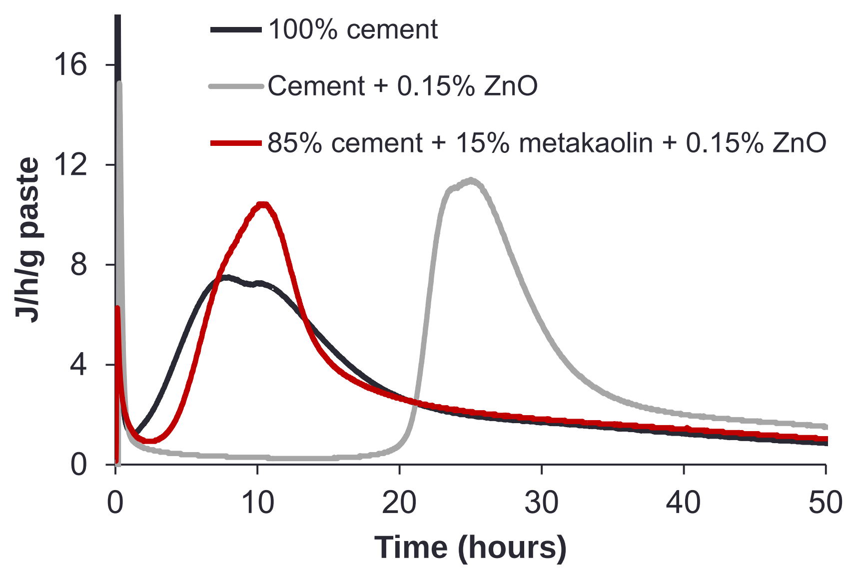
Effects of ZnO addition on Hydration



Co-calcination

Added separately





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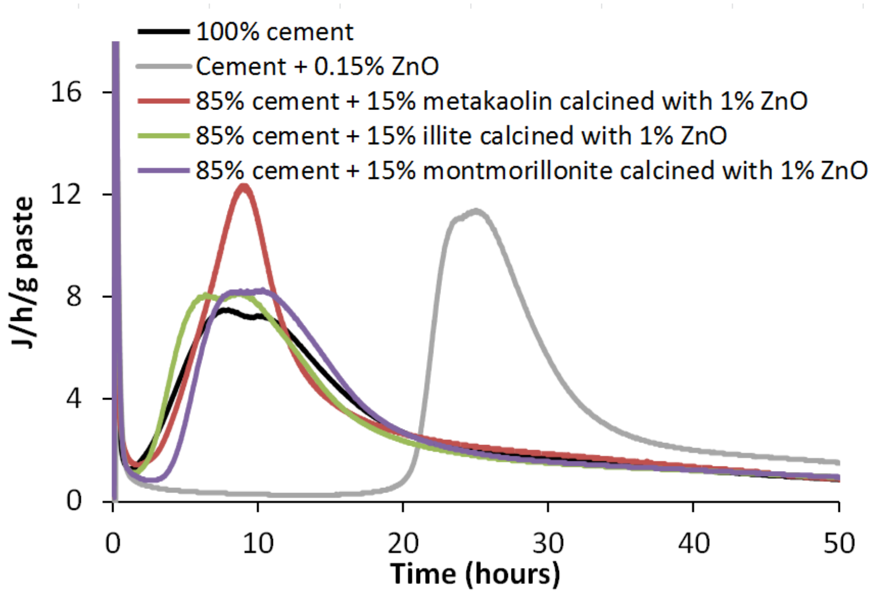

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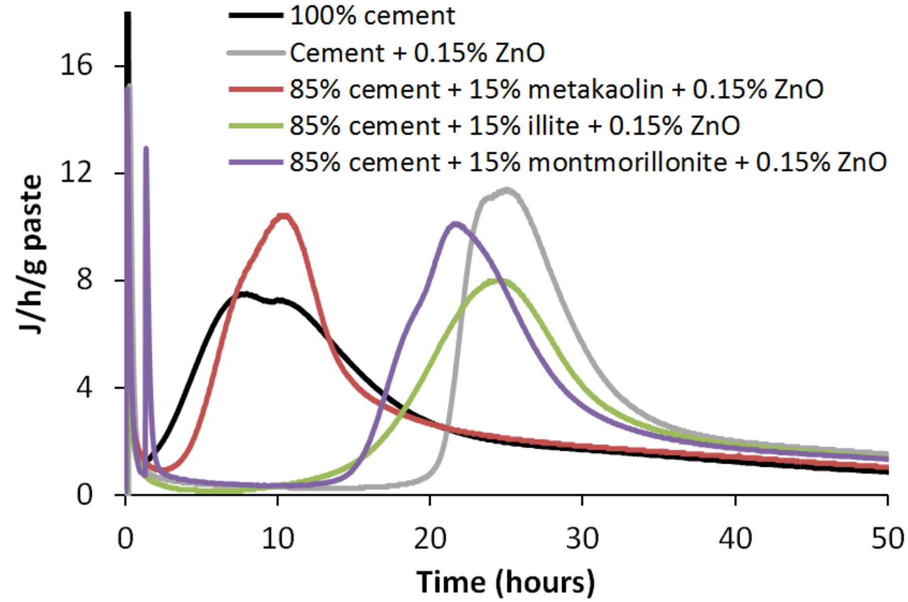

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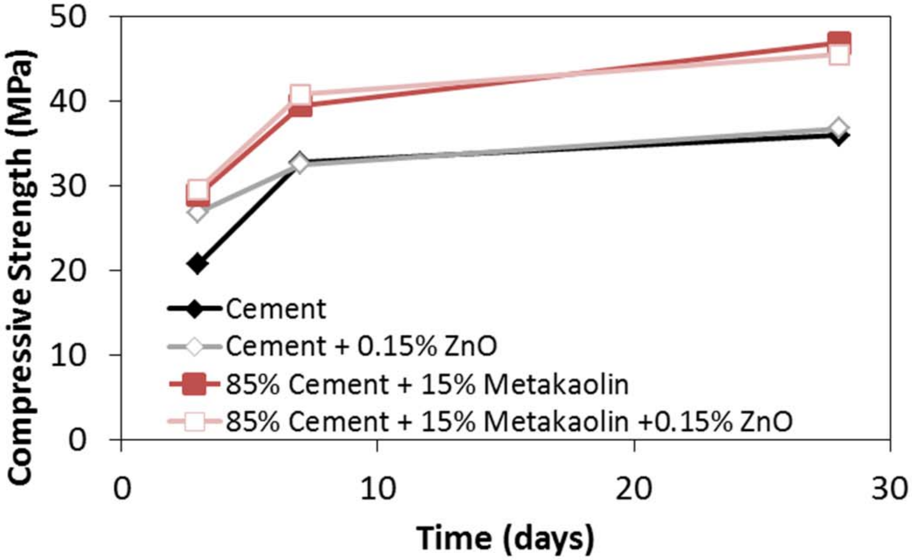
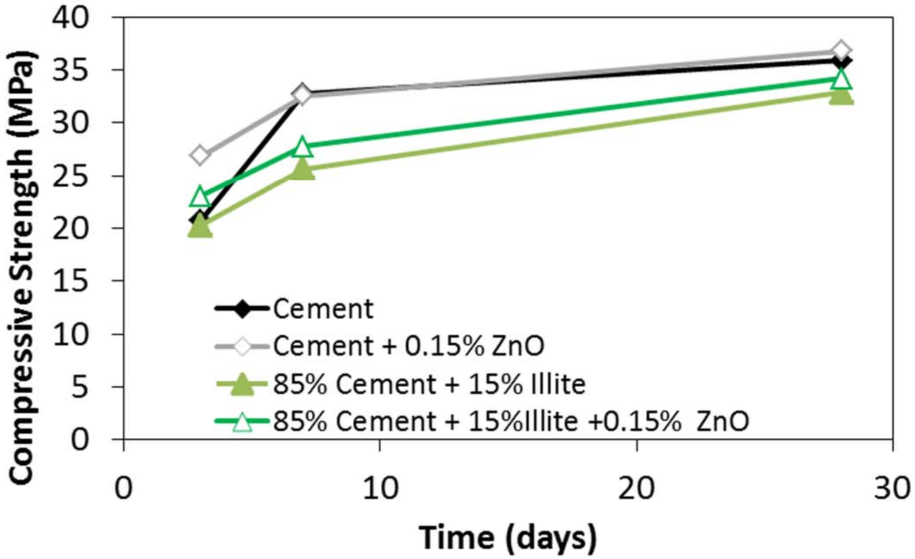
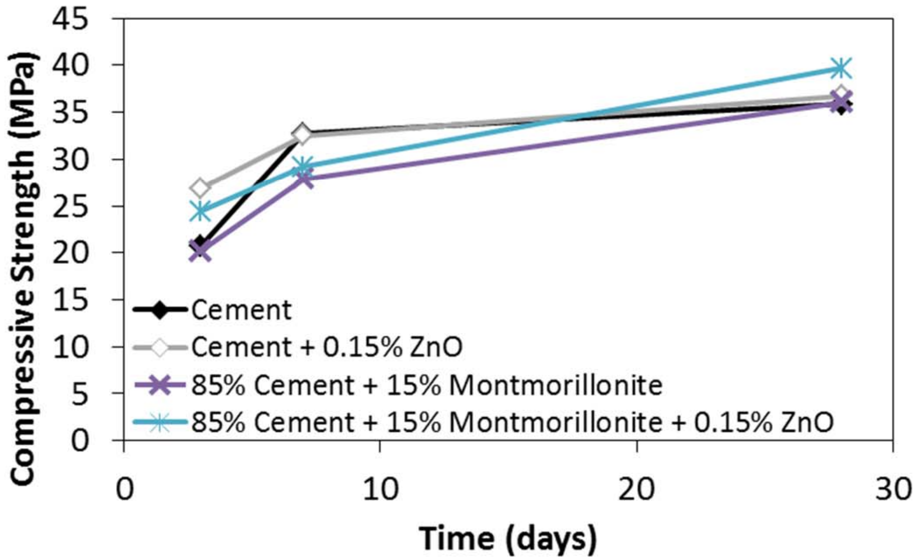
Compressive Strength







Summary and Conclusions

- Impure clays are plentiful and have an appropriate oxide composition for use as SCMs for portland cement concrete
- Challenges with these materials involve high water demand and low reactivity
- Both challenges can be addressed through calcination
- Reactivity is related to crystallinity and this can be addressed through chemical treatments in addition to calcination
- ZnO shows some promise of altering the reactivity of clays