Effect of Particle Size Distribution of Metakaolin on Hydration Kinetics of Tricalcium Silicate

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Introduction

- Metakaolin (MK) has been widely investigated and benefit the bulk properties and environmental costs of mortars and concretes due to MK's *filler* and *pozzolanic* effects. [1, 2]

—*Filler effect:* increases formation C-S-H gel promoting heterogeneous nucleation.

—*Pozzolanic effect:* SCM reacts with $Ca(OH)_2$ (i.e. CH) to form C-S-H gel.

- **Motivation:** How the filler and pozzolanic effects are affected by differences in surface reactivity is unknown unlike quartz or limestone [3].
- **Objective:** How does differences MK particle size distributions affect these mechanisms and C_3S hydration.

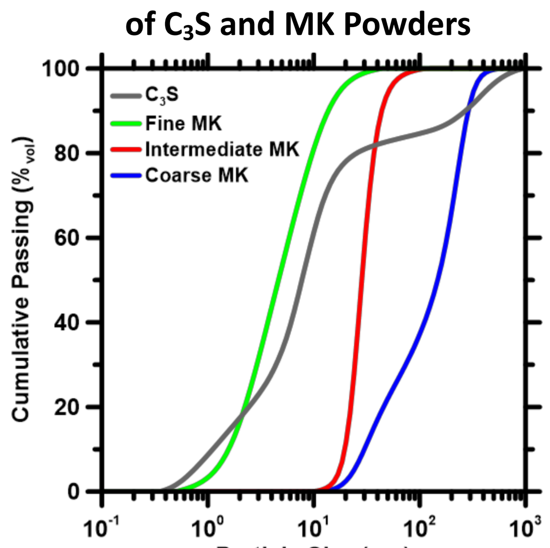
Material Preparation

- 99+% pure C_3S was synthesized to a 3:1 molar ratio of $CaCO_3$ and SiO_2 at 1500°C.
- Commercially available MK (Imerys Metastar HP501 — 99.1% pure) were separated into three (3) particle size distributions (PSDs) via wet sieving process per ASTM C325-07 standard.
- The median particle size (d_{50}) was measured using a static light scanning analyzer (Microtrac S3500); the specific surface area (SSA) was calculating from the d_{50}.
- MK does not rehydrate during the wet sieving confirmed via thermal analysis and X-ray diffraction.

Material Surface Characteristics

C_3S-SSA		=	562 m^2/kg
	Fine	=	672 m^2/kg
MK-SSA	Inter.	=	80 m^2/kg
	Coarse	=	29 m^2/kg

Particle Size Distribution (PSD) of C_3S and MK Powders



Experimental Procedure

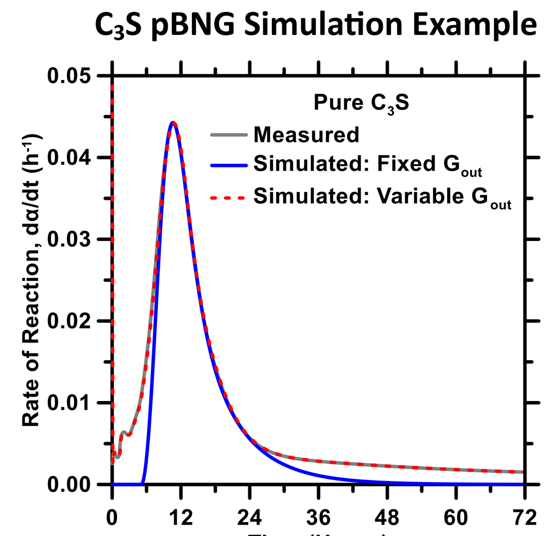
- Hydration kinetics of [C_3S + MK] pastes were prepared with l/s 0.45 for 72 hours in the TAM IV calorimeter at 20°C ± 0.1°C.

—Similar dissolution experiments were conducted with [CH + MK] pastes at a 1 : 1 molar ratio.

- Pastes were kept in isopropanol to arrest hydration before conducting thermogravimetric analysis.
- A modified phase boundary nucleation and growth model (pBNG) was implemented to extract product nuclei, allowing to evaluate effectiveness of MK.

TAM IV Calorimeter

C_3S pBNG Simulation Example



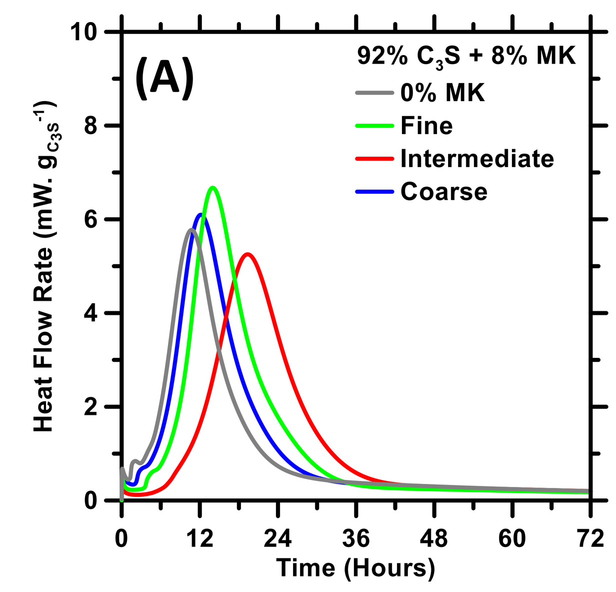
Experimental Results

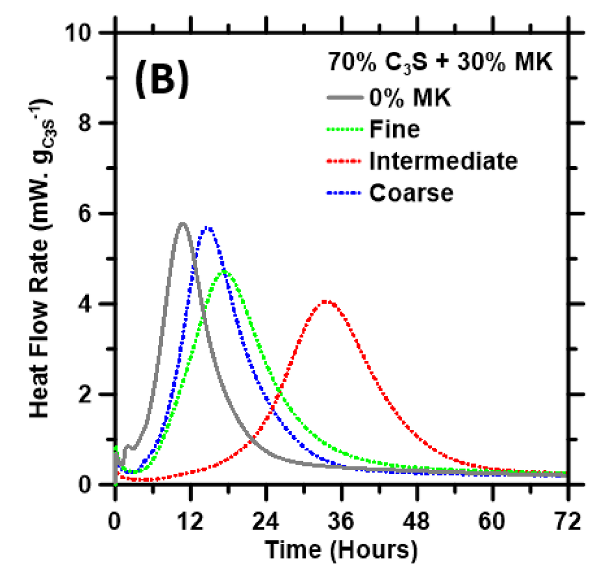
C_3S + MK Calorimetry—Effect of MK Size

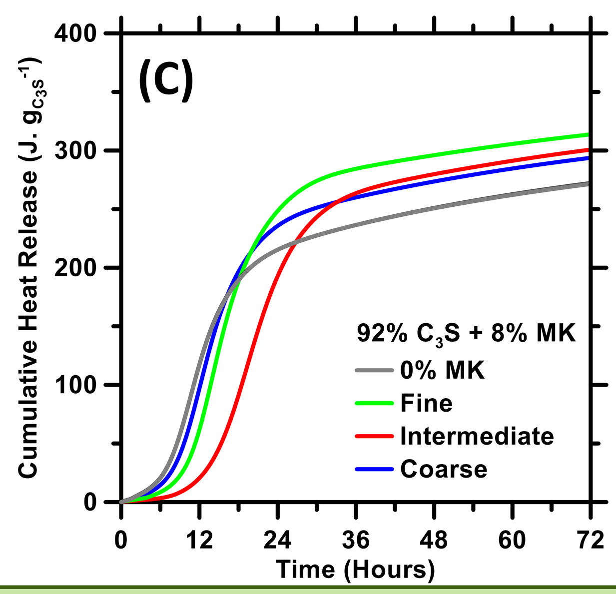
A. and B. Regardless of the MK PSD, the both 8% and 30% MK additions broadens the heat flow curves and delays the hydration peak.

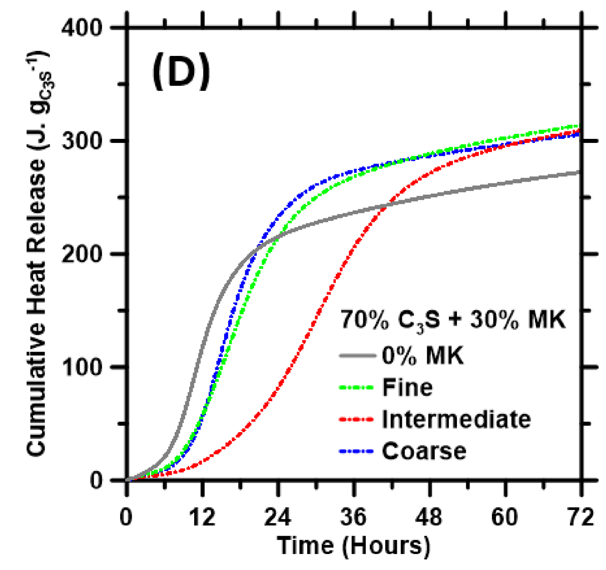
—The induction period duration increases with increasing MK dosage where the intermediate MK delays the peak the most.

C. and D. The addition of MK increases the cumulative heat release more so than the C_3S paste, approaching ≈ 300 J per gram of C_3S.



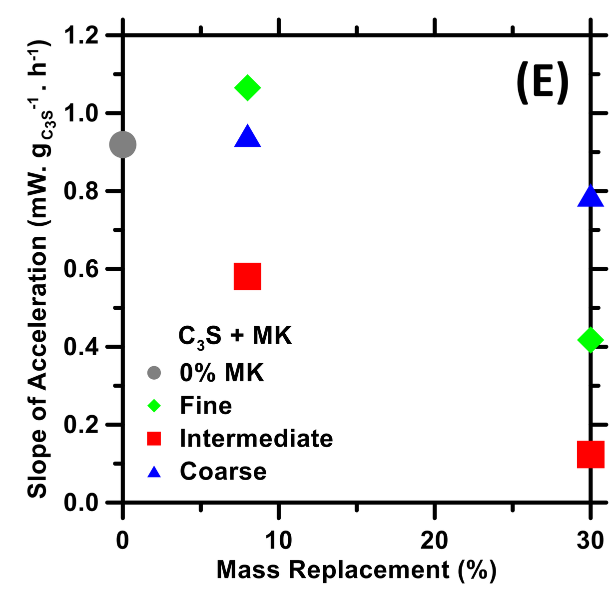


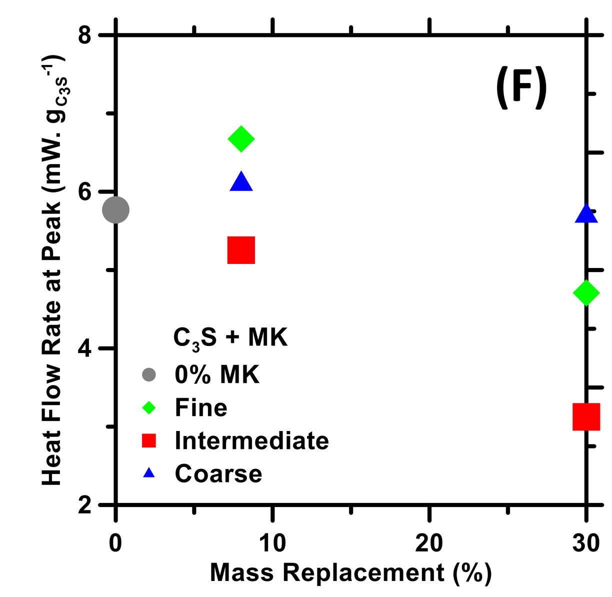




Extracted Calorimetry Parameters

E. and F. Low replacement level fine and coarse MK improves the slope acceleration and maximum heat flow rate indicating the *filler effect*. Larger additions of metakaolin reverse these benefits due to excess aluminate $[Al(OH)_4^-]$ ions. [4] Intermediate MK is more complicated and is explained below see below.



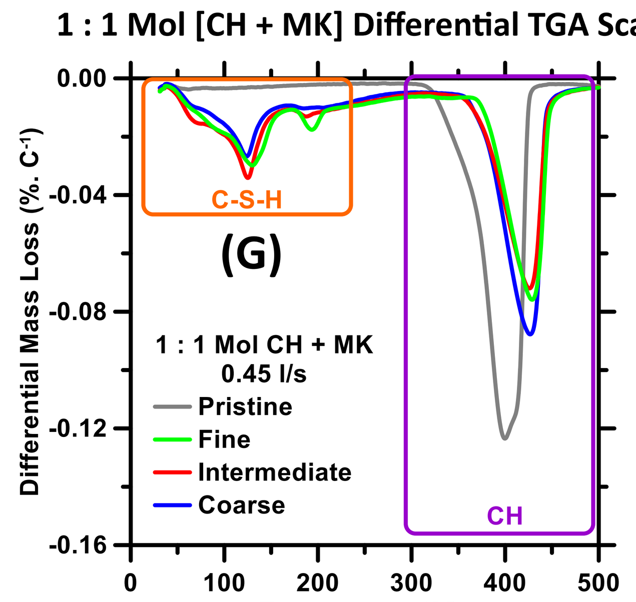


MK Pozzolanic Reactivity

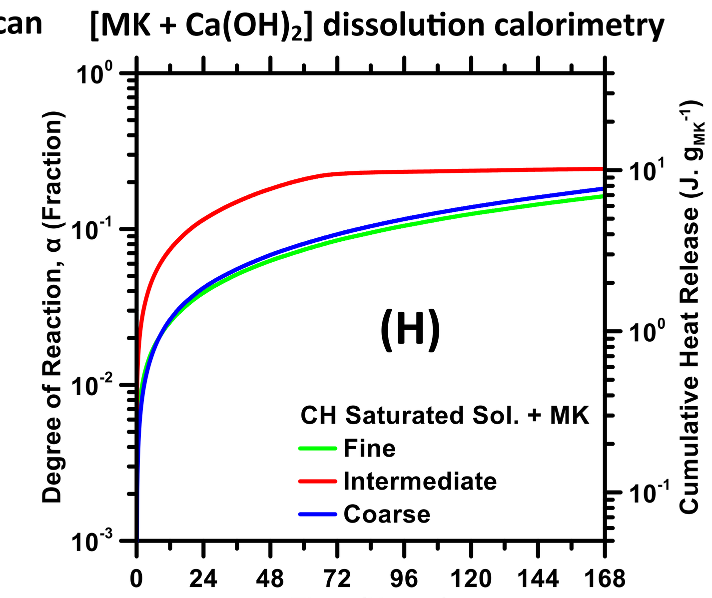
G. and H. At 1 : 1 molar ratio, the pozzolanic reaction with CH is substantial consistent with literature [1].

- The dissolution of [MK + CH] pastes is the greatest with intermediate MK which exhibits greatest dissolution facilitating the $[Al(OH)_4^-]$ ions to go into pore solution pacifying hydration.
- This is the reason why the intermediate [C_3S + MK] paste exhibits the greatest pacification during hydration.

1 : 1 Mol [CH + MK] Differential TGA Scan



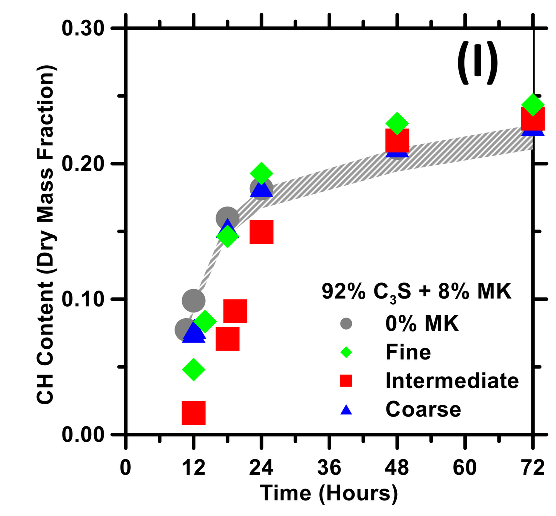
[MK + $Ca(OH)_2$] dissolution calorimetry

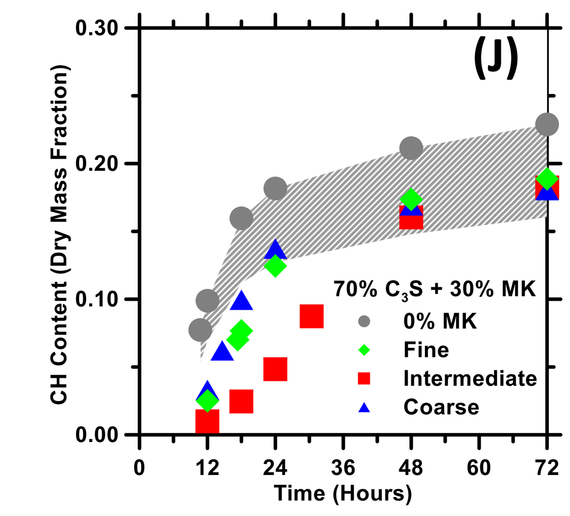


Simulation Results

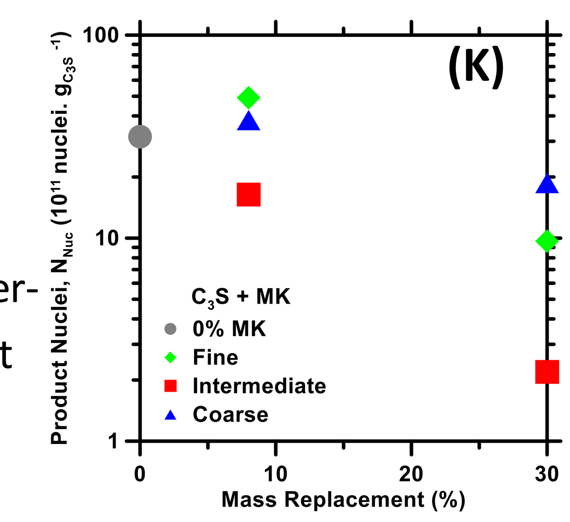
I. and J. The addition of [C_3S + MK] reduces the amount of CH below the dilution line (shown as grey area) during early ages suggesting that MK is delaying the hydration and is not rapidly reacting with CH.

- However, the CH content in [C_3S + MK] pastes is much lower than 1 : 1 [MK + CH] paste and at later ages pozzolanic reactivity is expected to increase.





K. The product nuclei (i.e. the amount of C-S-H per g C_3S) increases with 8% coarse or fine MK. This is indicative of *filler effect*. The larger doses and intermediate MK reverse this benefit shown by increase $[Al(OH)_4^-]$ ions by dissolution or dose.



Conclusions

- Unlike fillers such as limestone and quartz, the correlation between the specific surface area (SSA) on hydration of C_3S is nonlinear.
- MK is able to facilitate heterogeneous nucleation and growth of C-S-H, enhancing nucleation density (i.e. the amount of C-S-H) by *filler effect.*
- MK reacts significantly with CH but kinetics are slow in paste conditions.
- But the magnitude of these benefits is dependent on PSD and dosage level (MK< 10%).
- Higher doses of MK release aluminate $[Al(OH)_4^-]$ ions that pacify C_3S and MK particles inhibiting hydration.
- Low replacement of coarse (i.e. 10μm-100μm) MK due to slight filler effects while being least susceptible surface passivation and particle agglomeration.

References

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