Reactivity of Alternative Supplementary Cementitious Materials

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Open Topic Session

October 31, 2023

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Collaborators

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Supplementary Cementitious Materials

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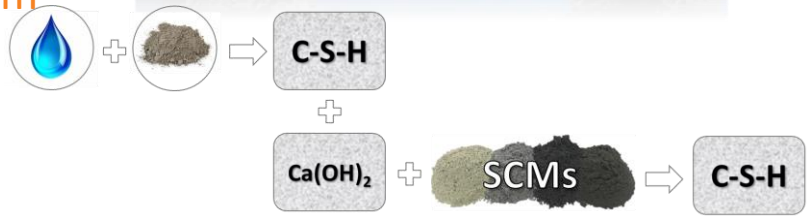
- Supplementary cementitious materials (SCMs) – Used to replace portland cement in concrete (5-70%).
- SCMs can improve concrete sustainability (CO_2 emissions) and durability (long-term properties).
- SCMs are typically by-products and waste products from other industries.
- SCMs are typically composed of amorphous calcium-aluminosilicate phases
  - Latent hydraulic: Can react with water, once activated
  - Pozzolanic: Need calcium hydroxide and water to react
  - Inert: Do not react in a latent hydraulic or pozzolanic manner



Snellings RILEM TL 2016, Suraneni and Weiss CCC 2017, Suraneni et al. CCC 2018, 2019

Reactivity Testing of SCMs

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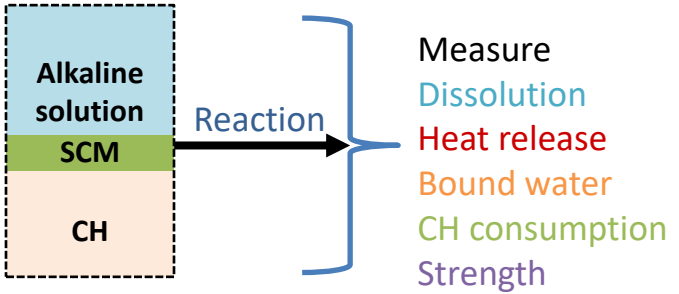
- Reactivity tests measure various aspects of SCM reactivity in model/cementitious systems under normal/accelerated conditions.
- Different reactivity tests in use
  - Strength activity index (ASTM C311) traditionally used in the United States and its variants
  - Based on lime consumption – Chapelle and Frattini tests
  - Modified lime strength test based on existing Canadian standards
  - Calcium hydroxide, bound water, heat release, strength, bulk resistivity of cement-SCM systems (paste/mortars)
  - R^3 (ASTM C1897) and modified R^3 tests.



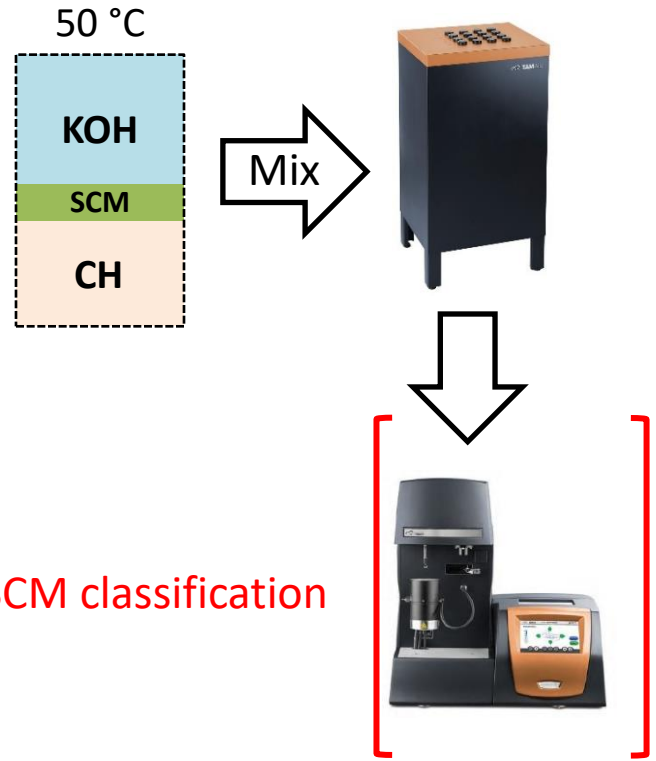
Measures of reaction in an SCM system of varying composition, with or without cement and sand

Can vary
Mixture proportions
Alkaline solution composition
Temperature
pH

Pourkhorshidi et al. CCC 2010, Ramanathan et al CCC 2020a,b, Snellings and Scrivener M&S 2016, Kasaniya et al. ACI Mater. 2019

Modified R^3 Test - Methodology

- A variant of the R^3 test – some differences.
- Calcium hydroxide (CH) to SCM ratio = 3:1
- Liquid-to-solid ratio 0.9, 0.5 M KOH (pH 13.5)
- Isothermal calorimetry at 50 °C for 10 days
- Thermogravimetric analysis at 10 days
- Heat release and calcium hydroxide consumption together can be used for classification

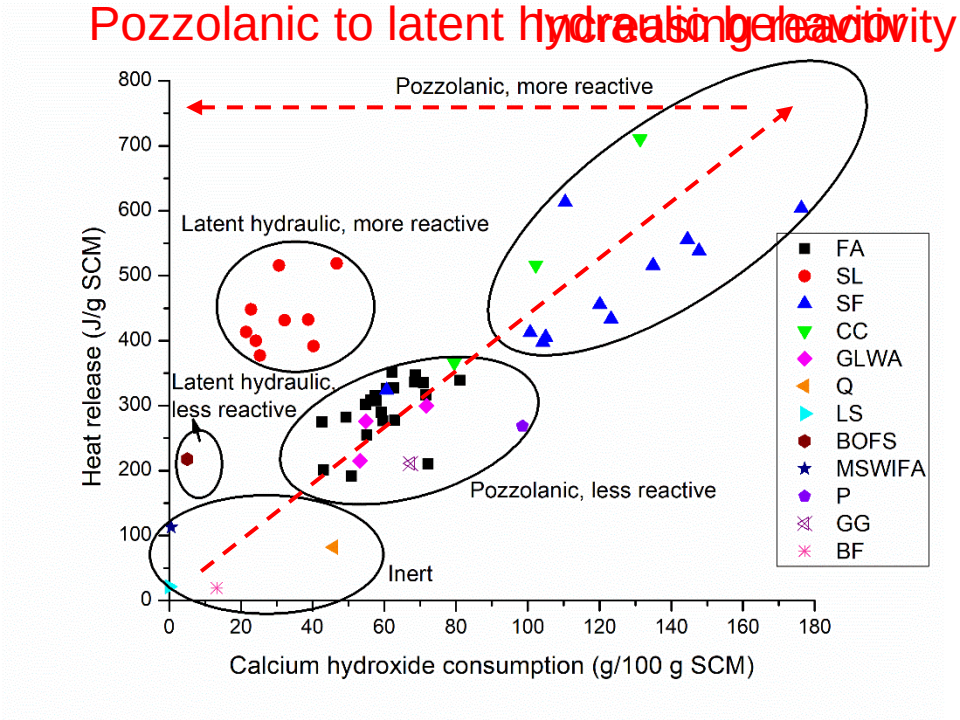


TGA for SCM classification

Suraneni and Weiss CCC 2017, Suraneni et al. CCC 2019

Outputs of Modified R³ Test

- More reactive SCMs farther away from the origin
- Distinction between:
  - Pozzolanic and hydraulic
  - Less and more reactive
- Reactivity "threshold" – 100 J/g SCM



Suraneni and Weiss CCC 2017, Suraneni et al. CCC 2019

Alternative SCMs evaluated

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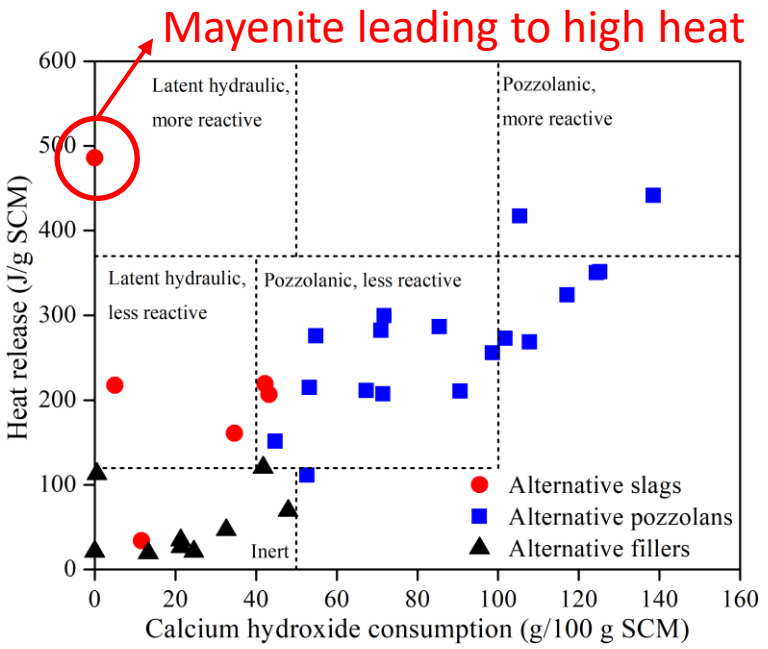
- **Slags**
  - Basic oxygen furnace slag (BOF), Ladle furnace slags (LF), Pig iron cupola furnace slags (PIC), Copper (CU) slag
- **Pozzolans**
  - Corn ashes (CCA/CSA), Rice husk ashes (RHA), Blended biomass ashes (BLA), Ground lightweight aggregates (GLWA), Glass powders (GP), Bottom ashes (BA), Natural Pozzolans (P, L)
- **Inert fillers**
  - Municipal solid waste incineration fly ash (MSWIFA), Basalt fines (BF), Sandstone filler (SST), Nepheline syenite filler (NF), Silica flour (SF), Limestone (LS), Mine tailings (MT)

Ramanathan 2021

Alternative SCMs Reactivity

- **Alternative slags** are generally either inert or less reactive.
- **Alternative pozzolans** show a wide range of reactivities depending on the material (very low to high reactivity).
- **Alternative filler** materials are inert, as expected.
- Material d_{50} mostly less than 45 µm and generally less than 75 µm



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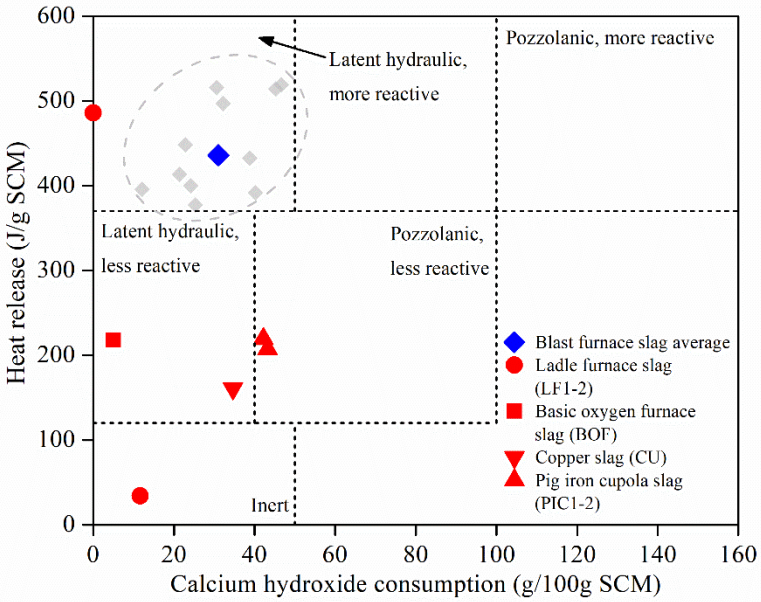
Reactivity of Alternative Slags

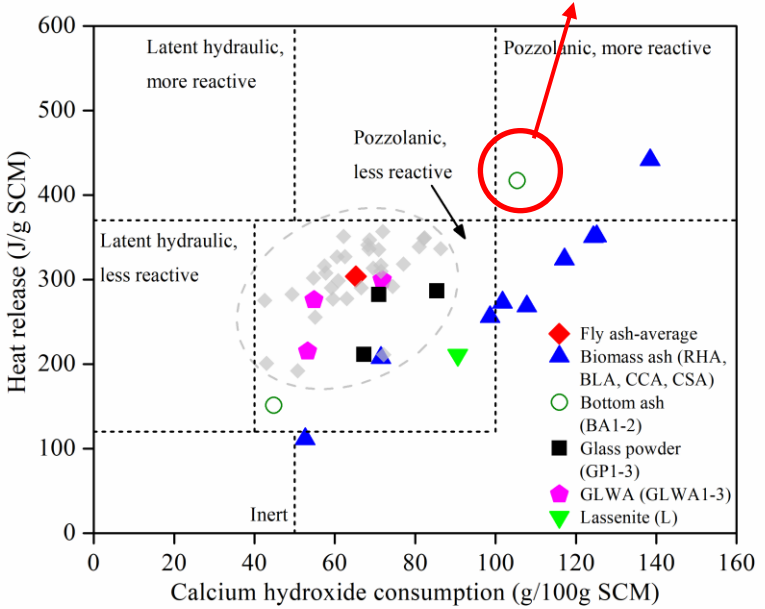
- **LF** generally inert – crystalline; mayenite ($C_{12}A_7$) in LF2 causing high heat release.
  - Low strengths when used as SCM – sulfate imbalance observed.
- **BOF** – less reactive.
  - Reactivity from phases like alite and β-C_2S.
  - Presence of CaO, MgO a concern.
- **CU** – crystalline and generally inert
- **PIC** are less reactive – lower CaO contents compared to other slags
  - Possible beneficiation with calcining based on literature.
- **Treatment methods** to potentially improve reactivity – grinding, particle separation, heat treatment etc.,



Ramanathan 2021, Wang and Suraneni 2019

Reactivity of Alternative Pozzolans

- Generally **comparable or better reactivity than fly ashes** (shown in grey).
- **Biomass ashes** – range of reactivities – depending on particle sizes, pre-treatment methods, high unburnt carbon.
  - Potential issues in concrete – high P_2O_5, high alkali.
- **BA** – Lower reactivity compared to fly ash, grinding improved reactivity.
- **GP** – pozzolanic, grinding improved reactivity.
  - Replacement levels chosen with caution - variable composition – could affect their ability to mitigate alkali silica reaction

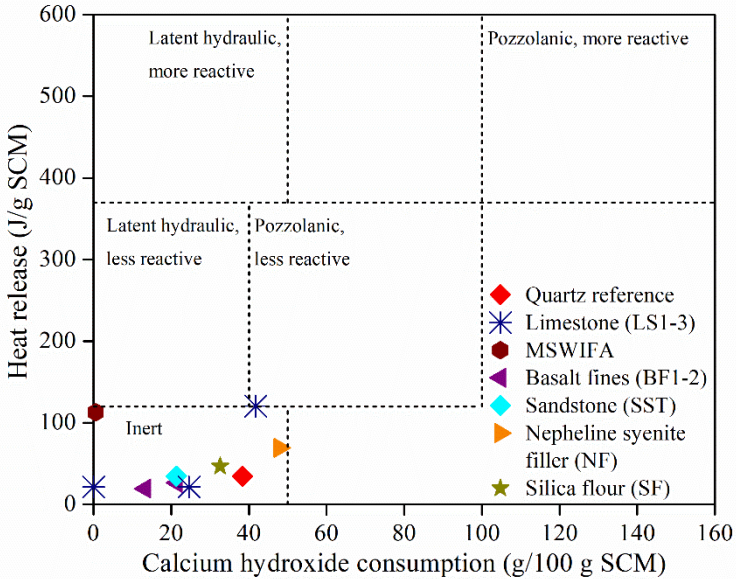


Beneficiation – Washing, grinding, ignition, etc.,

Ramanathan 2021, Ramanathan et al 2019, 2020a, 2020b, Shakouri et al 2020a, 2020b

Alternative Fillers

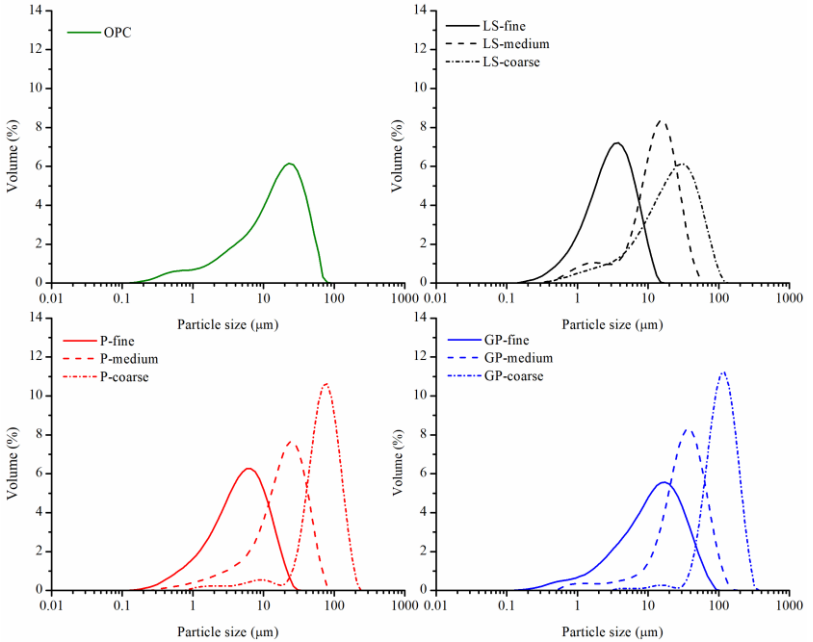
- **Generally inert**.
- Have secondary benefits
  - Example - Synergy of LS with aluminates in concrete.
- **MSWI ash** – Unreactive,
  - Can improve reactivity –
  - Quite complex - chlorides, metallic aluminum, heavy metals.
- **Basalt fines** – inert as is
  - Beneficiation through high temperature treatment and mechanochemical activation.
- Work in progress.



Ramanathan 2021, Wang and Suraneni 2019

SCM Fineness and Paste Properties

- Objectives of the study –
  a) Understand the effect of SCM d_{50} on modified R^3 test outputs
  b) Understand the effect of SCM d_{50} on cementitious paste properties at early and later ages (30% SCM, w/cm = 0.40)
  c) Assess if fineness impacts are similar for different materials and different properties
- Three SCMs tested, two pozzolanic and one inert



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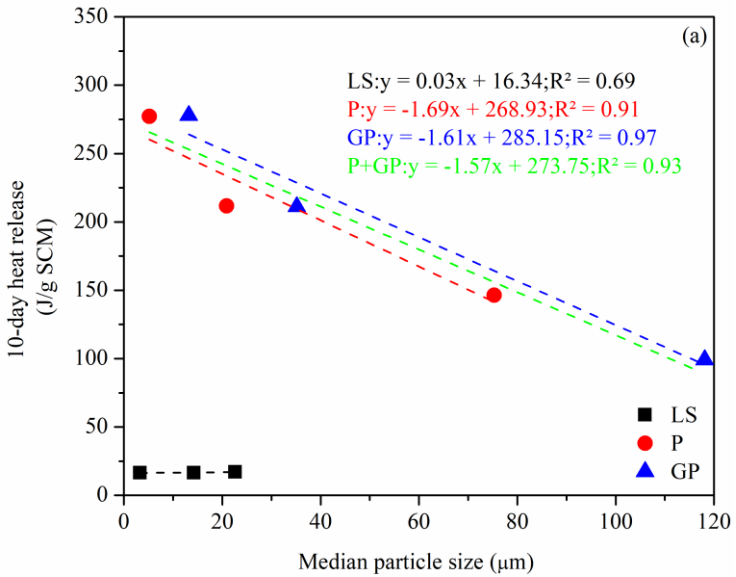
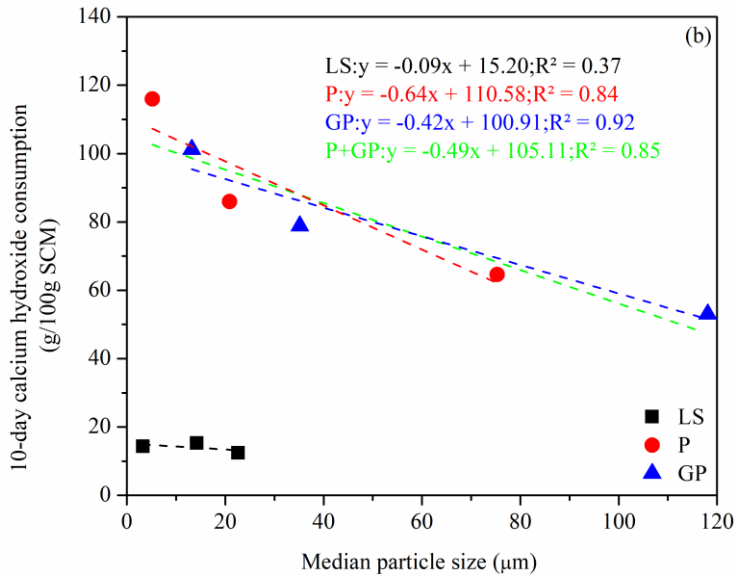
SCM Fineness and Modified R^3 Test Outputs





- For pozzolanic SCMs, reactivity increases (linearly) with fineness
- No impact for inert limestone
- P and GP have similar similar slope values

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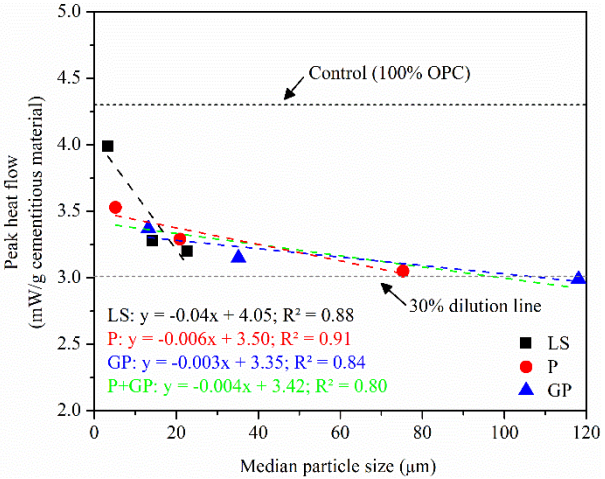
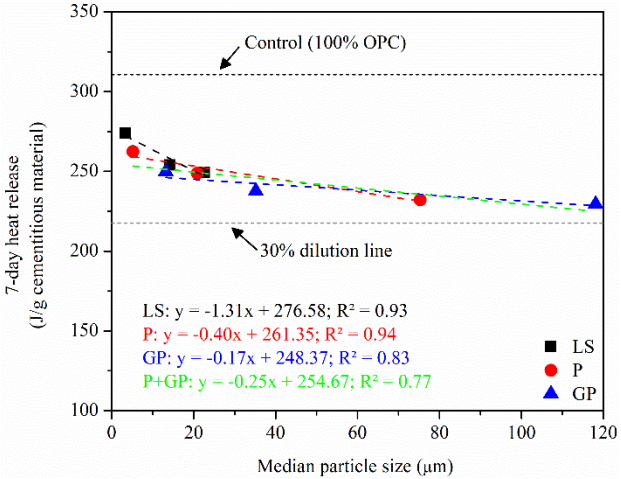
SCM Fineness and Paste Heat





- Peak heat flow and heat release increase with fineness
- Pure dilution for coarser SCMs, filler effect and reaction for finer SCMs
- LS clearly has a different level of filler effect

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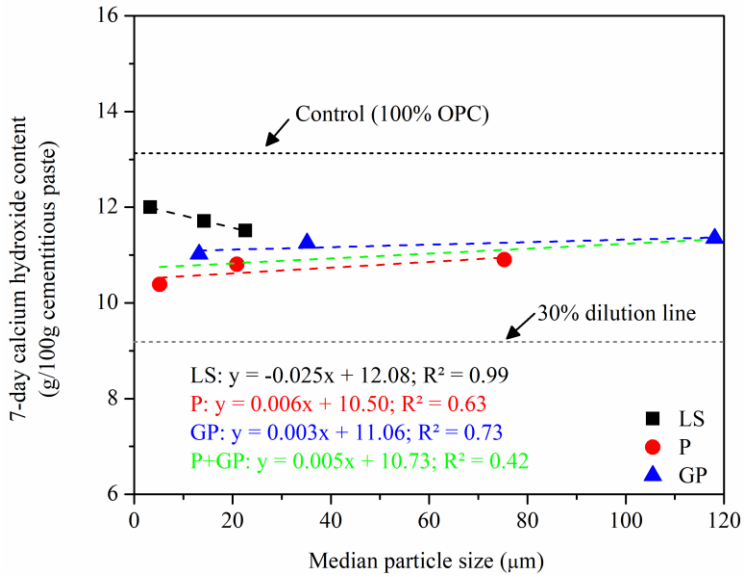
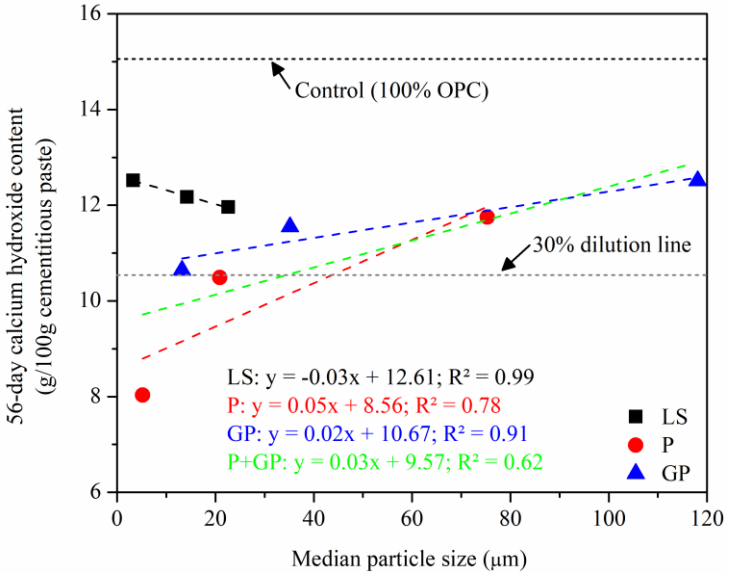
SCM Fineness and Paste Calcium Hydroxide

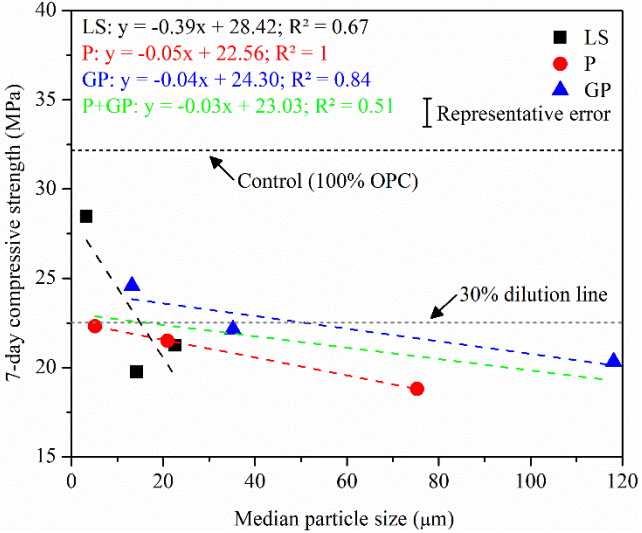


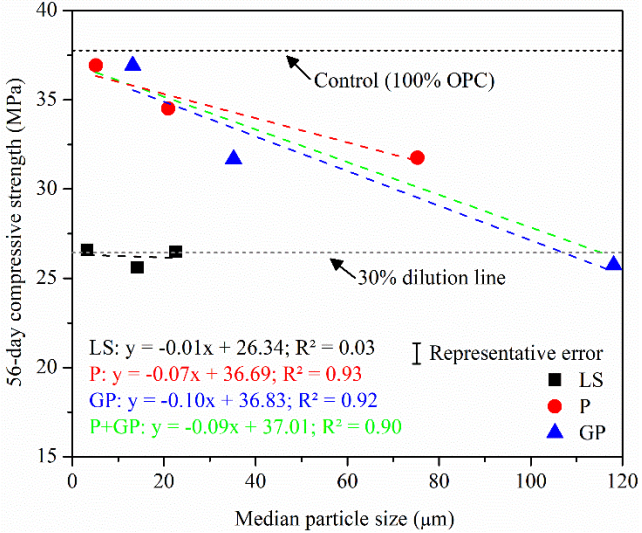


- Filler effect causes higher calcium hydroxide content at 7-days than expected from dilution
- Effects of reactive SCMs evident at later ages, higher replacement levels, higher fineness
- Inert LS has negative slope (no reaction)

Ramanathan 2021, Ramanathan et al 2022

SCM Fineness and Paste Compressive Strength



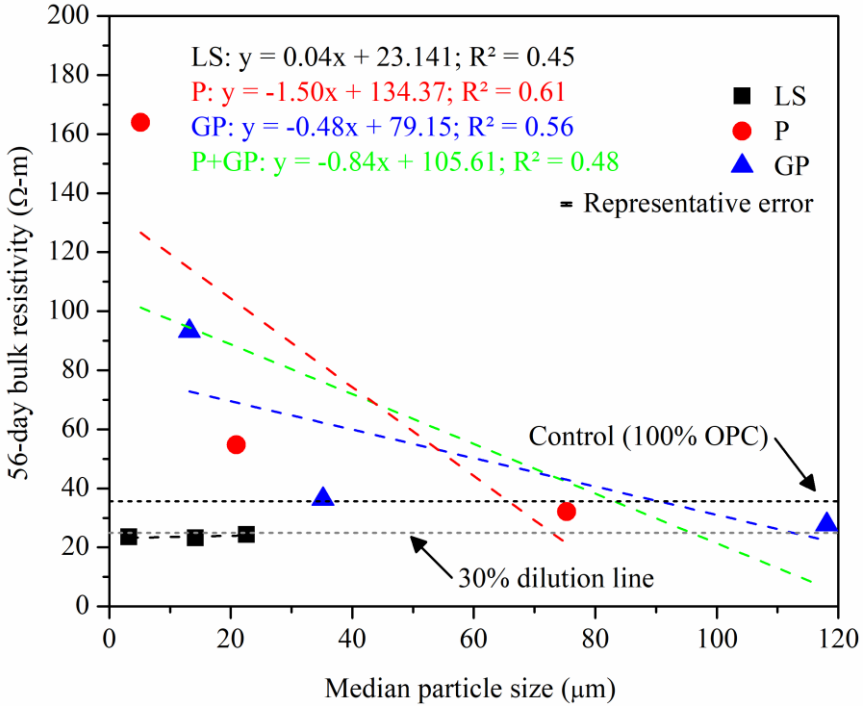


- Dilution dominates at early ages but some impact of fineness also seen
- Strong effects of fineness/reactivity seen at later ages: coarser SCMs largely show dilution, finer SCMs show reaction also
- Inert LS – No effect after early ages; pure dilution at 56 days

Ramanathan 2021, Ramanathan et al 2022

SCM Fineness and Paste Bulk Resistivity

- Early ages – No SCM effect on bulk resistivity
- Clear difference between reactive and non-reactive SCMs seen at 56 days – resistivity increases with fineness for reactive materials
- Pore refinement, pore solution and alkali binding changes, etc.
- At very low fineness levels, reactive SCMs can appear to be inert



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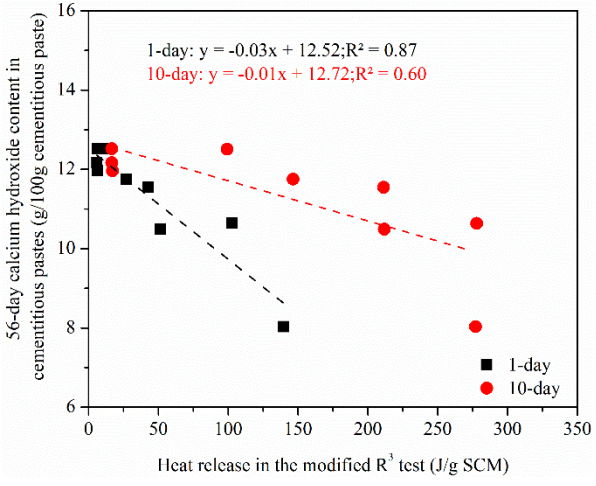
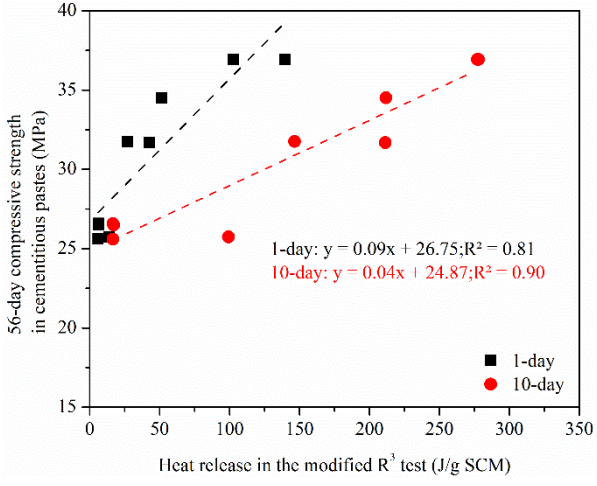
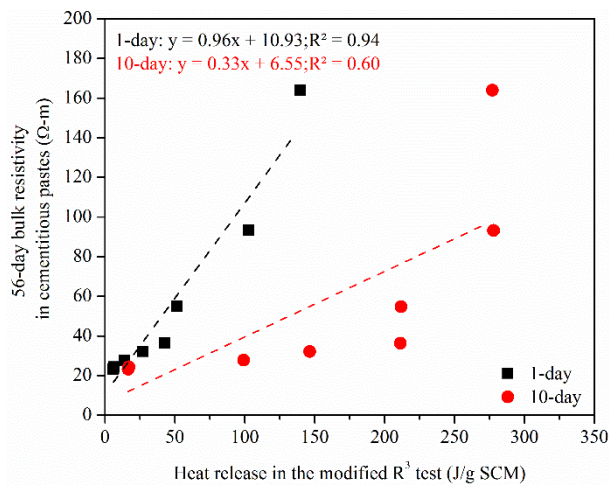
SCM Fineness and Paste Properties







- Strong correlations of 1-day modified R^3 test heat release with 56-day paste calcium hydroxide content, compressive strength, and bulk resistivity
- Limited number of points but make a case for modified R^3 test predicting later-age cementitious paste behavior

Ramanathan 2021, Ramanathan et al 2022

Conclusions

- **Reactivity tests alone cannot be used for assessing SCMs**. Full material classification required – XRD, XRF, PSD.
- **Marked increase in SCM reactivity** when comparing coarse P/GP vs fine P/GP, no change for LS – direct measure of reactivity from the modified R^3 test.
- Different effects at early and later ages in pastes – **filler effects at early ages and pozzolanic effects at later ages for P/GP**.
- **Beneficiation using various methods** – washing, thermomechanical, and mechanochemical activation are promising.


THANK YOU
QUESTIONS?