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COLLEGE OF ENGINEERING | School of Civil and Construction Engineering

Slag and Portland Limestone Cement: A Symbiotic Relationship

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Performance of Slag Cement with Portland-Limestone Cement in Concrete

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- Early-age performance of slag cement with Type IL cement has been found to be equal to or better than with Portland cement from the same source. The alumina in the slag cement can react with more of the finely divided limestone to form additional carboaluminate hydrates that then results in reduced porosity and increased early-age strength. There is also reduced permeability, as indicated by ASTM C1202 test results.
- While some early published papers indicated a potential concern for an increased risk of low-temperature thaumasite sulfate attack, our extensive long-term tests on concretes have shown that Type IL cement- slag cement combinations are as resistant to sulfate attack as Type I cement-slag cement combinations and more resistant than equivalent w/cm concretes made with Type V cements to both the ettringite and thaumasite forms of degradation.

Performance of Slag Cement with Portland-Limestone Cement in Concrete

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- This presentation will include discussion on these two topics and will also look at some recent projects with these materials. Speakers will walk through different reaction rates such as resistivity and diffusion with portland limestone cements, strength results and modeling.
- Learning Objectives:

  (1) Identify the differences in portland limestone cement, slag cement, and how they work to reduce the carbon impact of concrete;

  (2) Analyze relevant research and data related to the use of slag cement and portland limestone cement;

  (3) Explain how portland limestone cement and slag cement combinations create concrete structures that are more resistant to sulfate attack;

  (4) Identify different testing methods and case studies to illustrate the benefits of using these materials.

Why PLC and Slag?

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Jason Weiss, Edwards Distinguished Professor, Oregon State University

WHO ARE YOU?

Who Are You ?

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- Do you want to make your concrete better?
- Do you want to do your part to reduce carbon footprint?
- Do you want to try something with a high probability of success?

- Lets see if we can provide something of use for you!


Where do you start?

Cement & CO_2 Production

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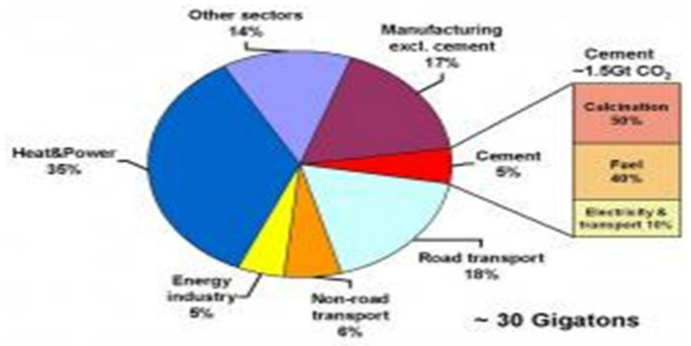
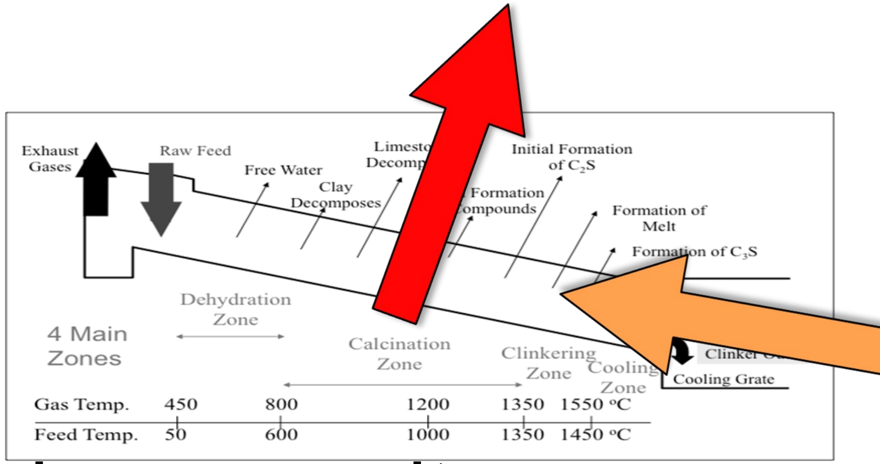
- You will hear cement accounts for 7-8% of global CO_2 (Mehta 1998)
- What/Where is the CO_2 coming from
  - Calcination (50%)
  - Combustion (40%)
  - Transportation (10%)

$$CaCO_3 \xrightarrow{\text{yields}} CaO + CO_2$$

$$C + O_2 \xrightarrow{\text{yields}} CO_2$$



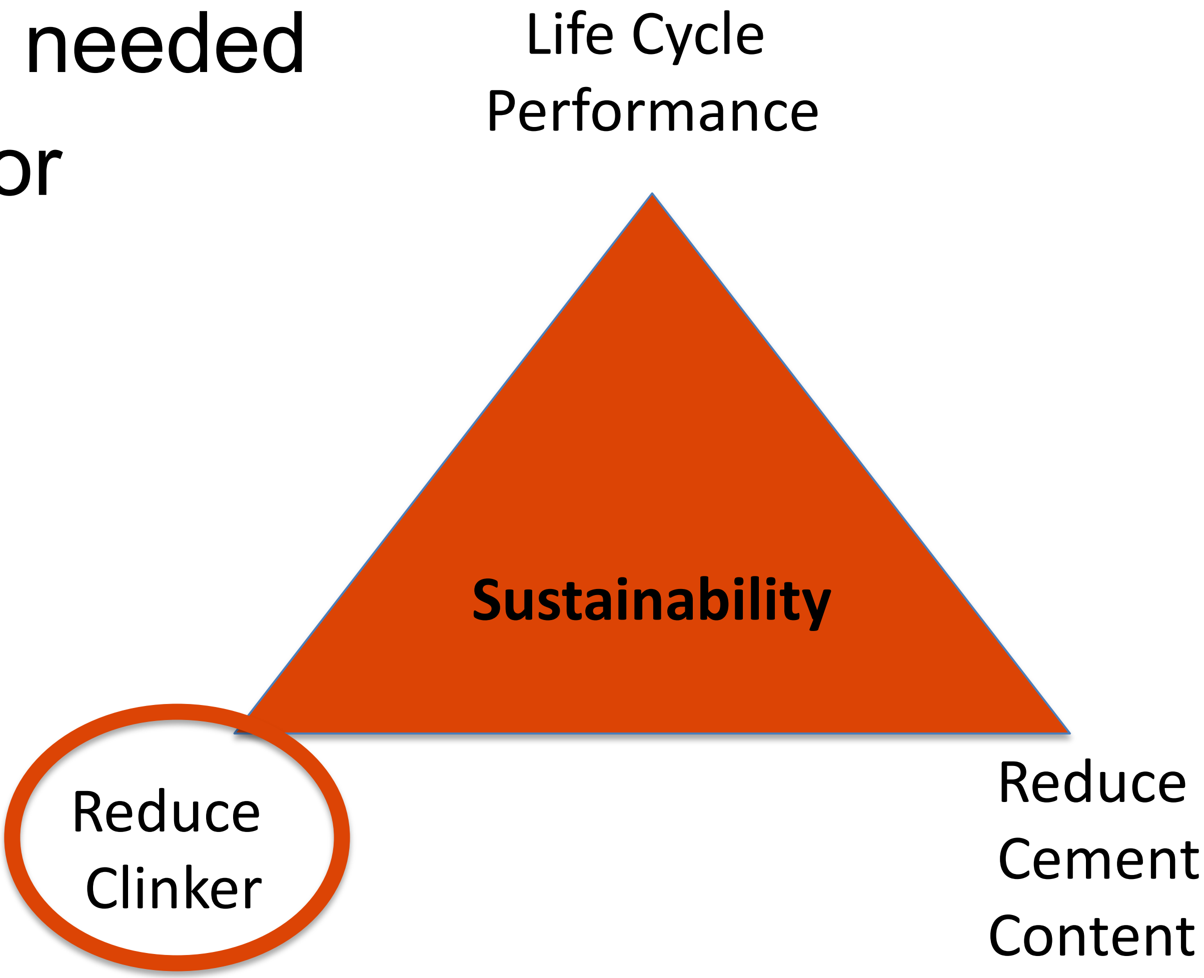


- Concrete has relatively low carbon emission per unit; however widespread use of concrete makes it a major contributor to manmade CO_2 emissions

Concrete Sustainability

- I will suggest that change is needed
- I will suggest that the time for change is

- Three Prong approach



Which Cement and Why

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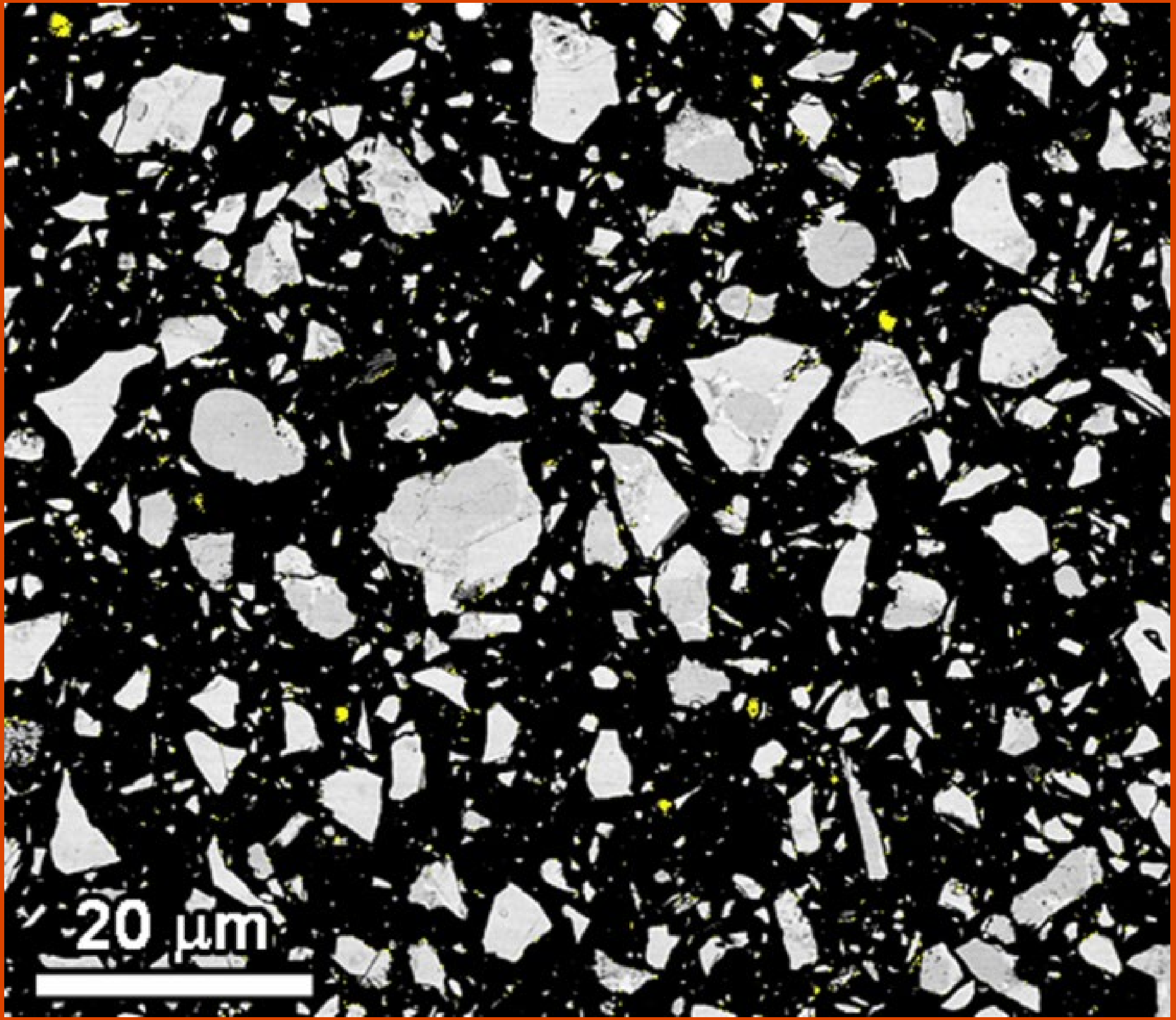

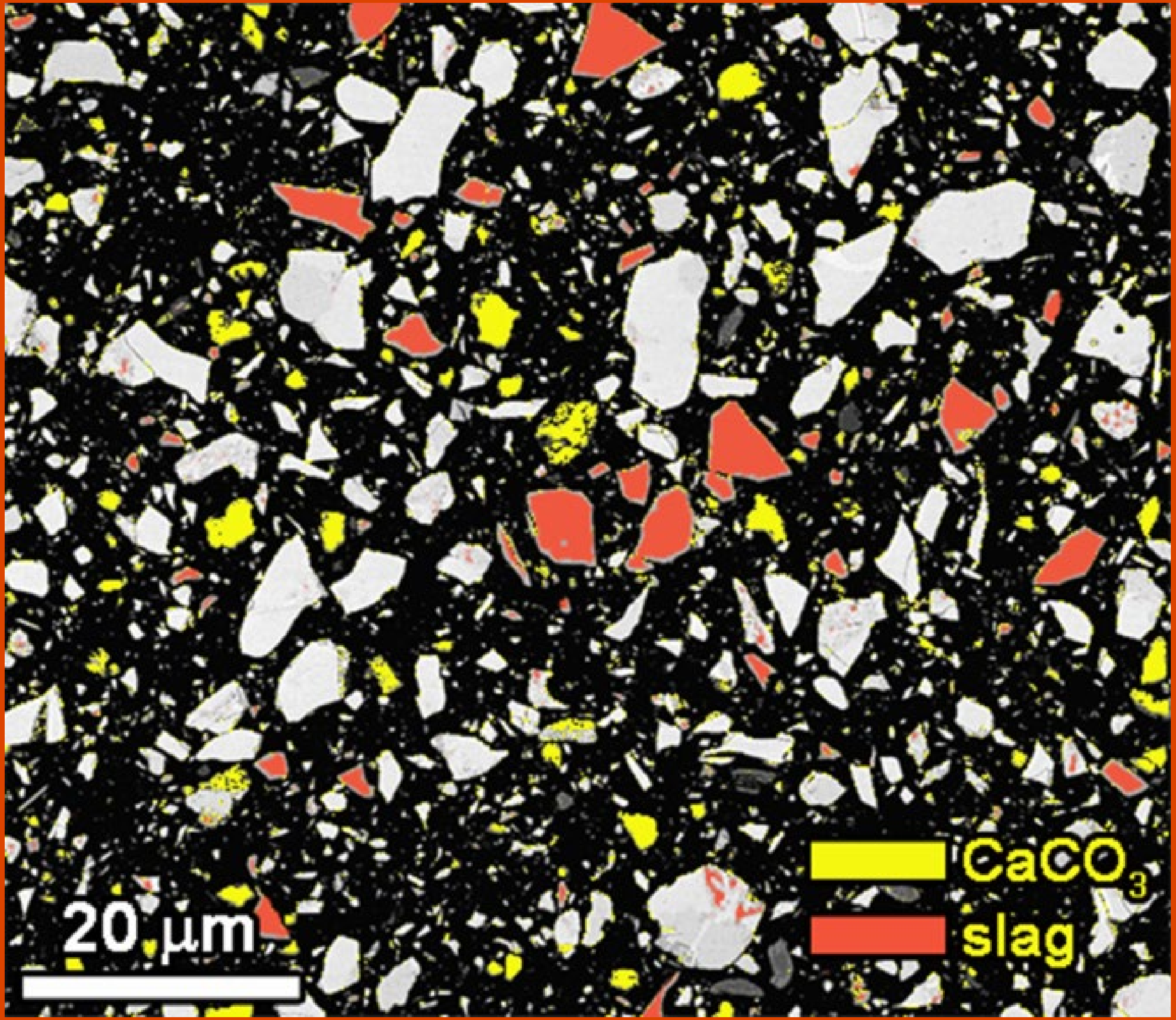

Lets compare cement

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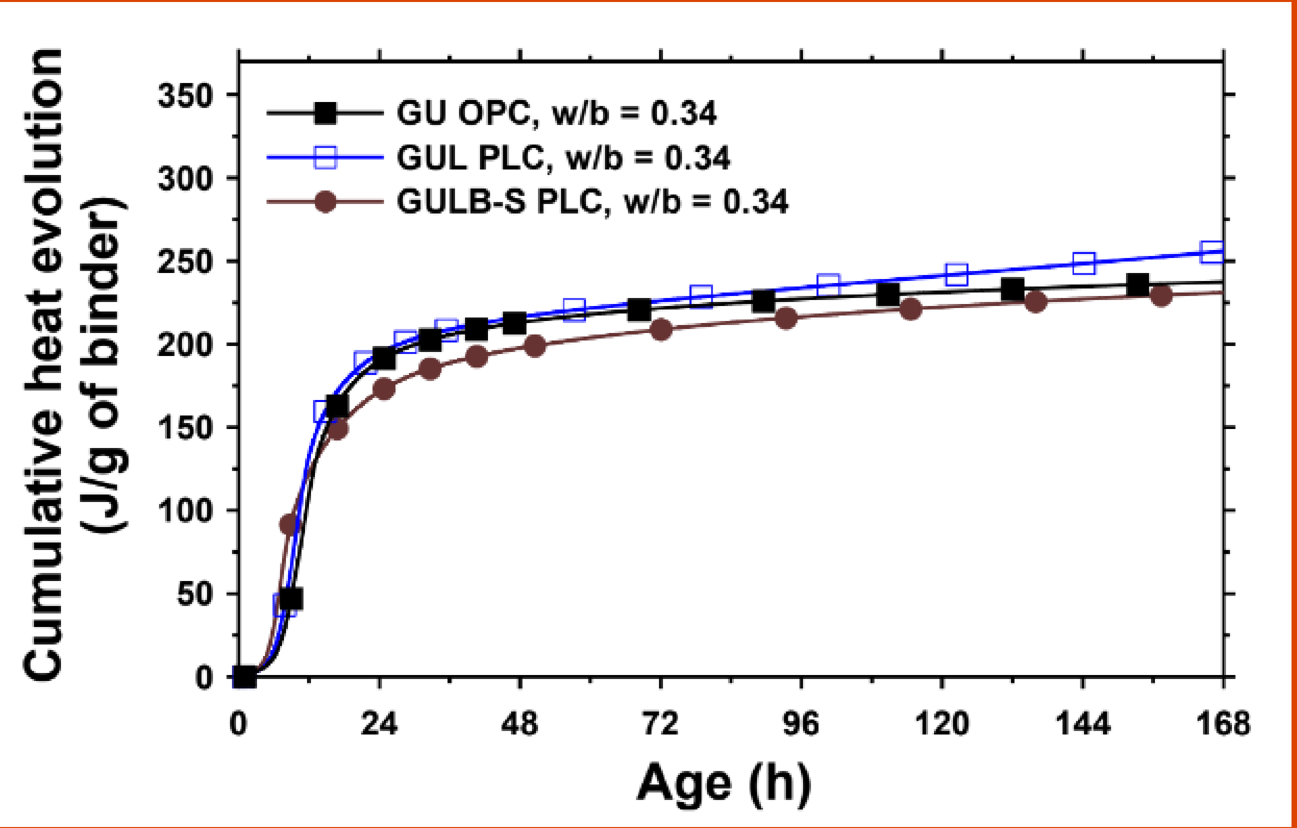
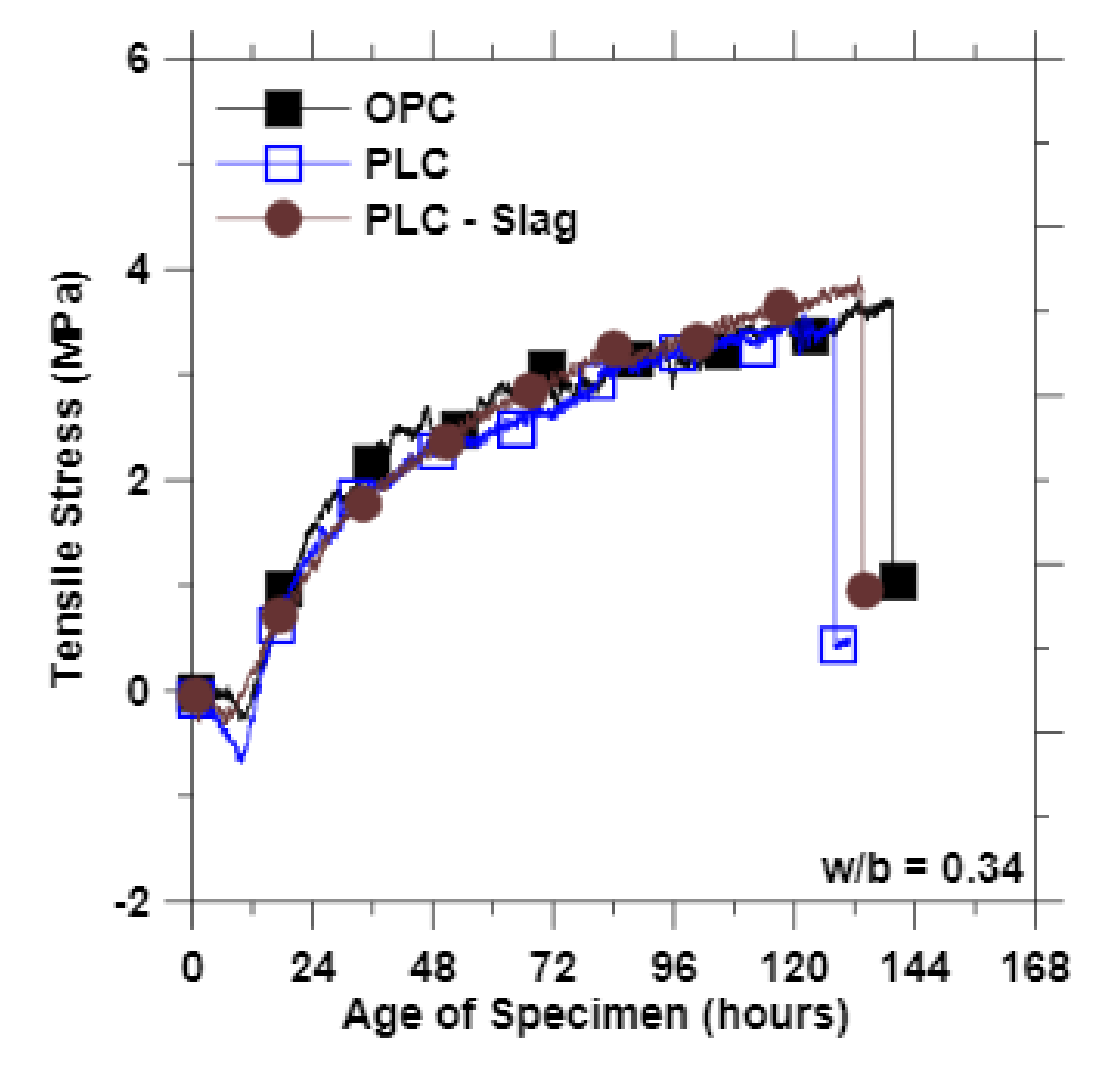
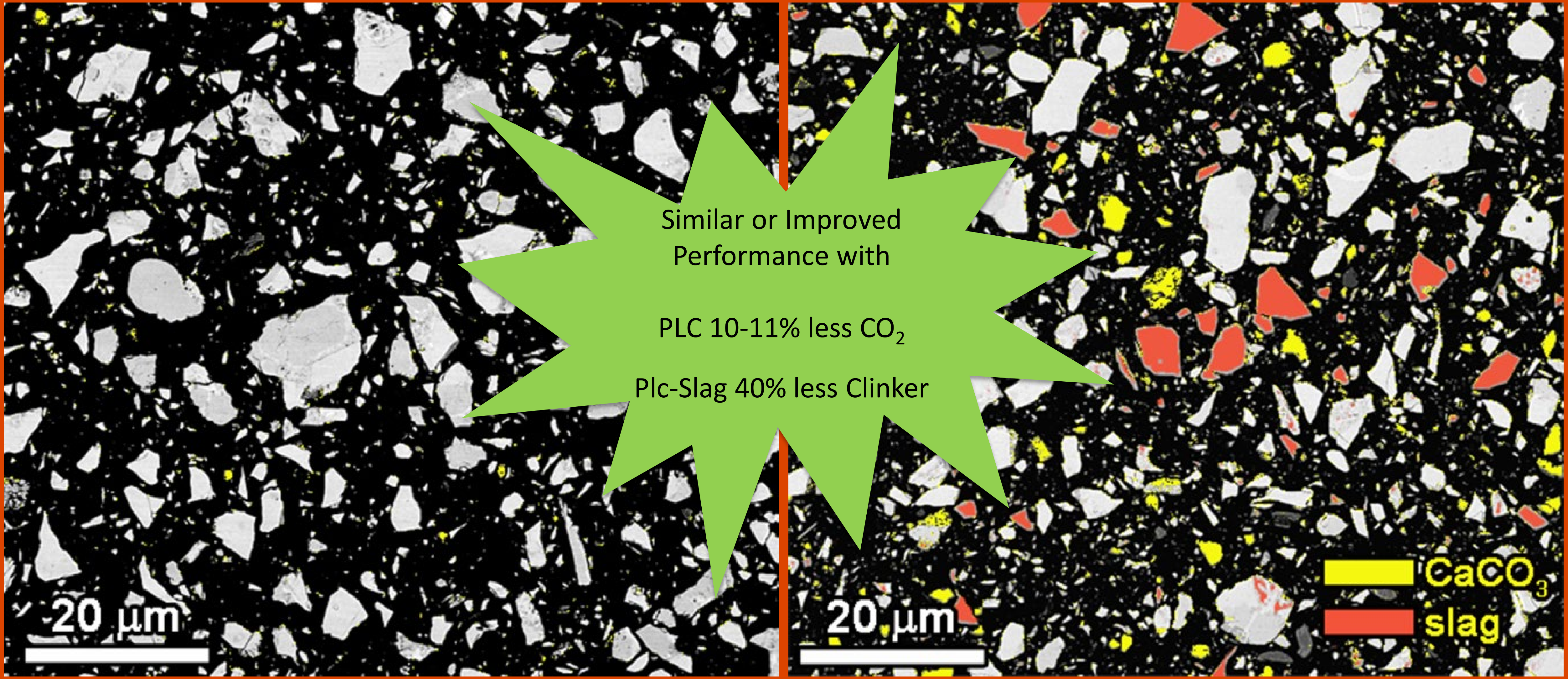




Similar strength (GULB-S PLC) slightly higher
Similar transport (GULB-S PLC) slightly improved

Which Cement and Why



Similar or Improved Performance with

PLC 10-11% less CO_2

Plc-Slag 40% less Clinker

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Ordinary Portland Cement
Versus
Portland Limestone Cement

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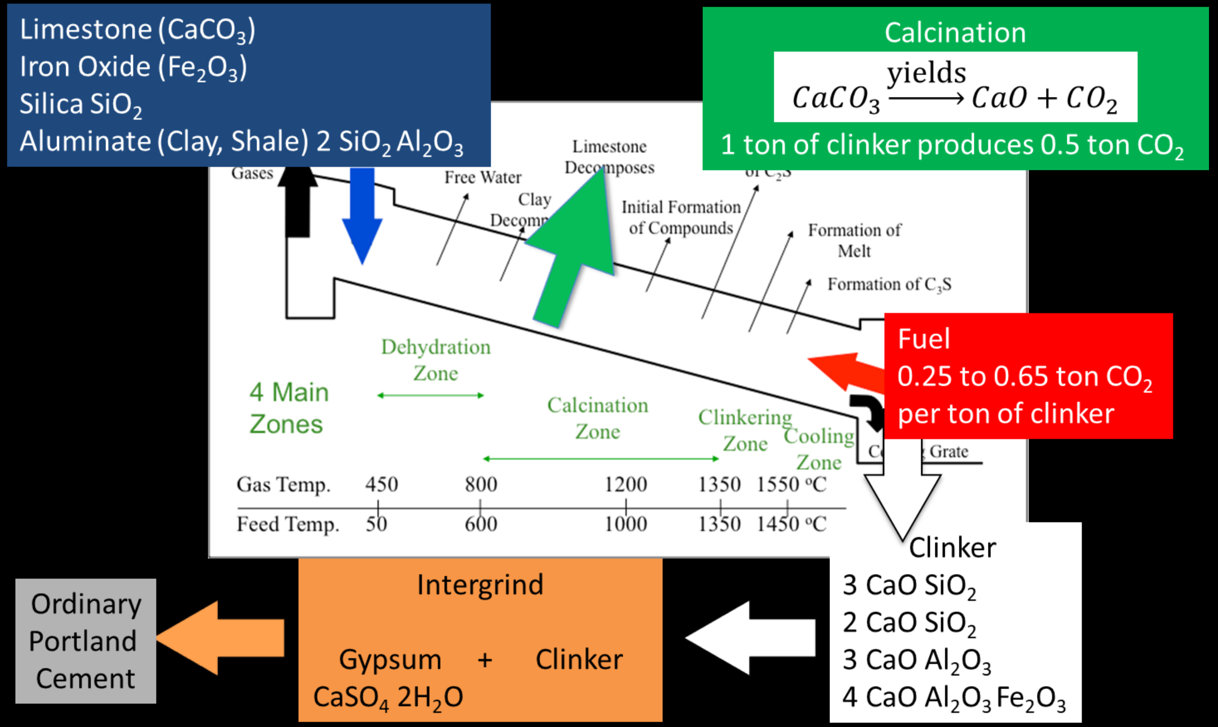
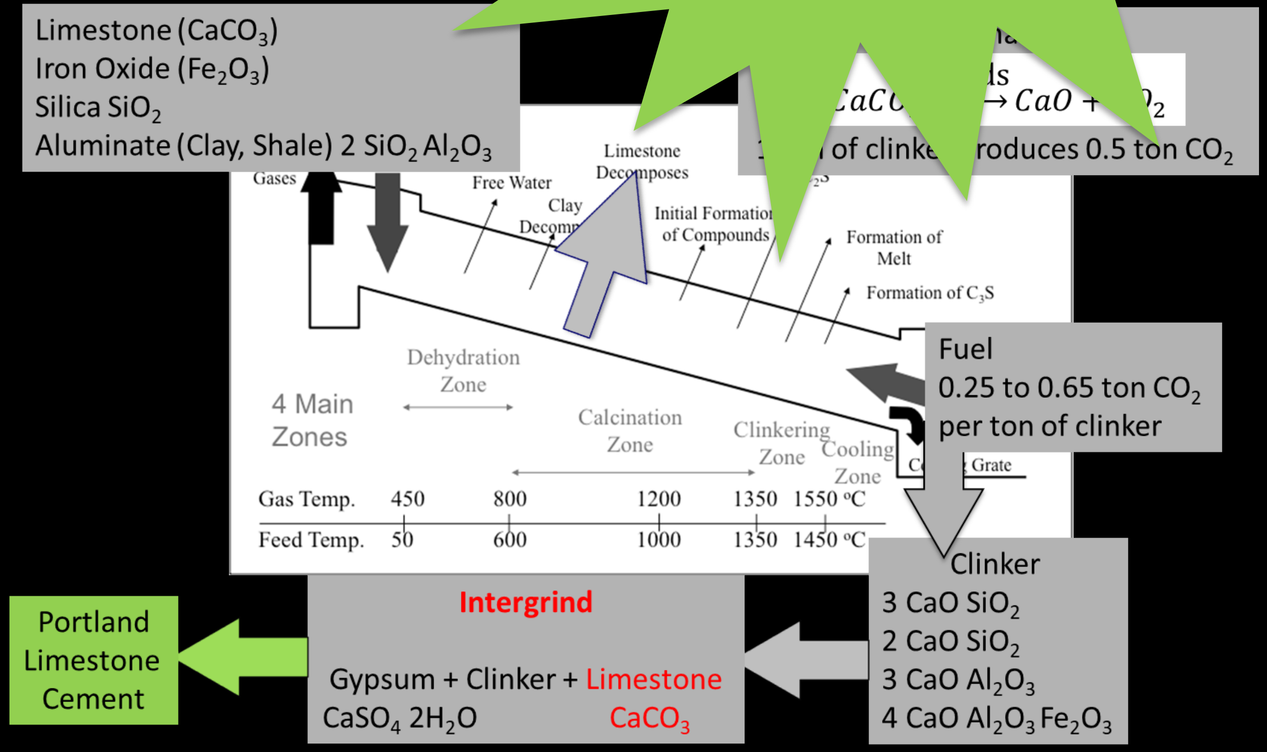
Very doable

In fact doneable, awaiting specification





When Dizzy Asks "Can We Fix It" Yes we Can!

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Very doable

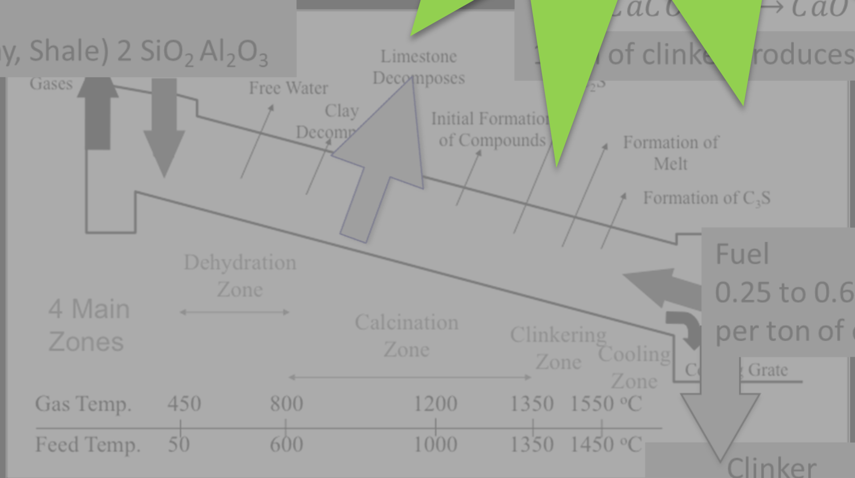
In fact doneable, awaiting specification

Limestone ($CaCO_3$)
Iron Oxide (Fe_2O_3)
Silica SiO_2
Aluminate (Clay, Shale) 2 SiO_2 Al_2O_3

Calcination

$$CaCO_3 \xrightarrow{\text{yields}} CaO + CO_2$$

1 ton of clinker produces 0.5 ton CO_2



Fuel
0.25 to 0.65 ton CO_2 per ton of clinker

Clinker
3 CaO SiO_2
2 CaO SiO_2
3 CaO Al_2O_3
4 CaO Al_2O_3 Fe_2O_3

Intergrind

Gypsum + Clinker + Limestone
$CaSO_4$ $2H_2O$ $CaCO_3$

Portland Limestone Cement

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Peanut
Butter

Slag and Portland Limestone Cement: ~~A Symbiotic Relationship~~

The Peanut Butter Cups That Make Concrete Better

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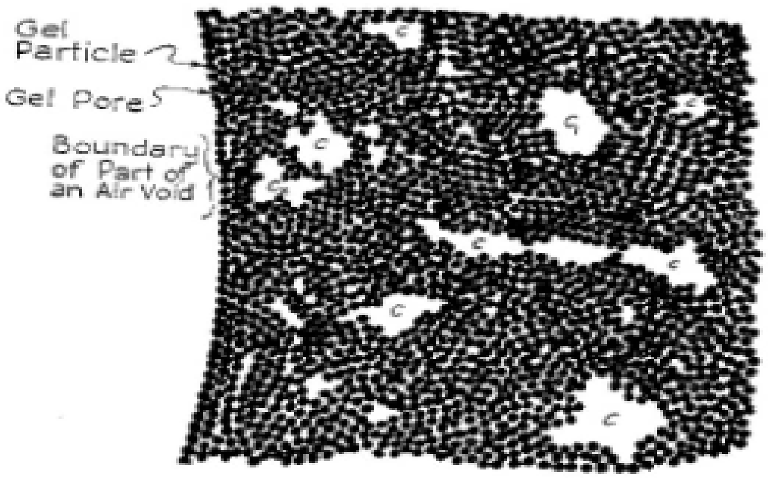
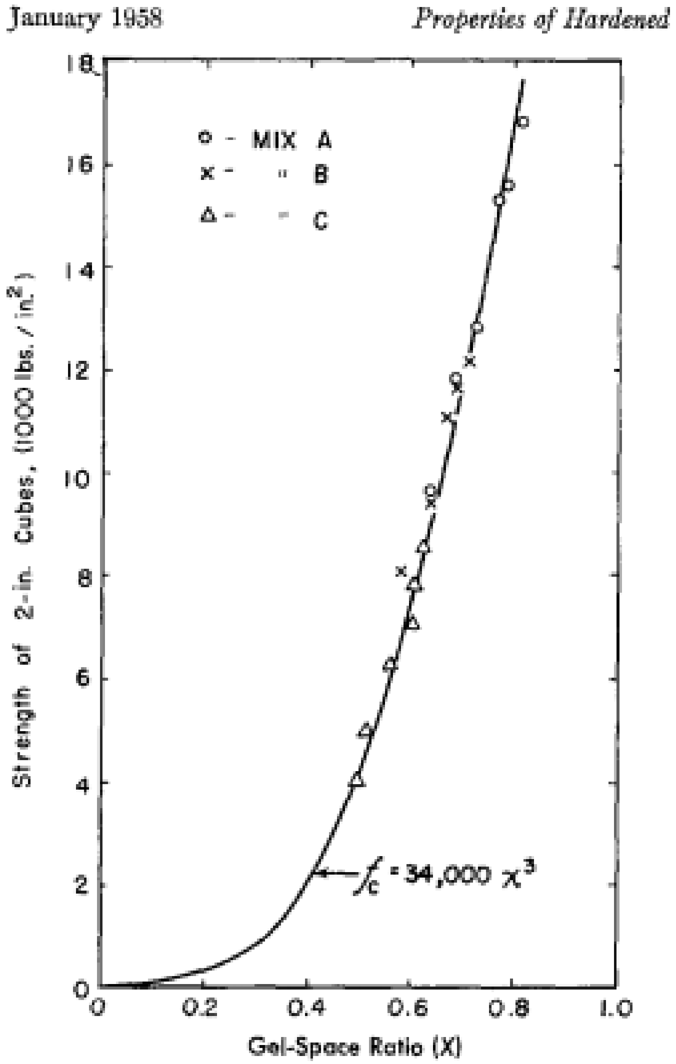
Pore Structure

- Pores are important
- They describe strength, transport, shrinkage, freeze-thaw
- Model developed by Powers and Brownyard



- Gel pores are the pores in the C-S-H gel (2-5 nm)
- Capillary pores (5 nm-10 μm) are the remnants of the space between the cement particles



PLC & the Porosity Plot

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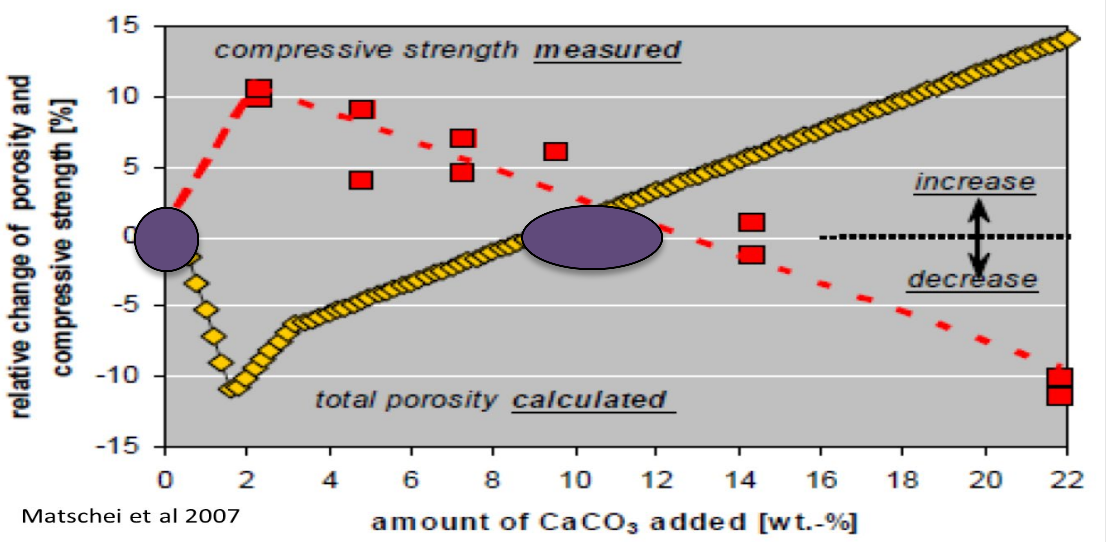
- The work by Matschei is a bit like the 'North Star' – Lets match no limestone performance
- Many people look at a plot like this and say 'ah' I get it, lets have a 'similar system at 28 days'
- Where does a plot like this come from
- How does this plot 'change' when we look at systems that are more complicated



Matschei et al 2007

Graphical Version of Powers Model

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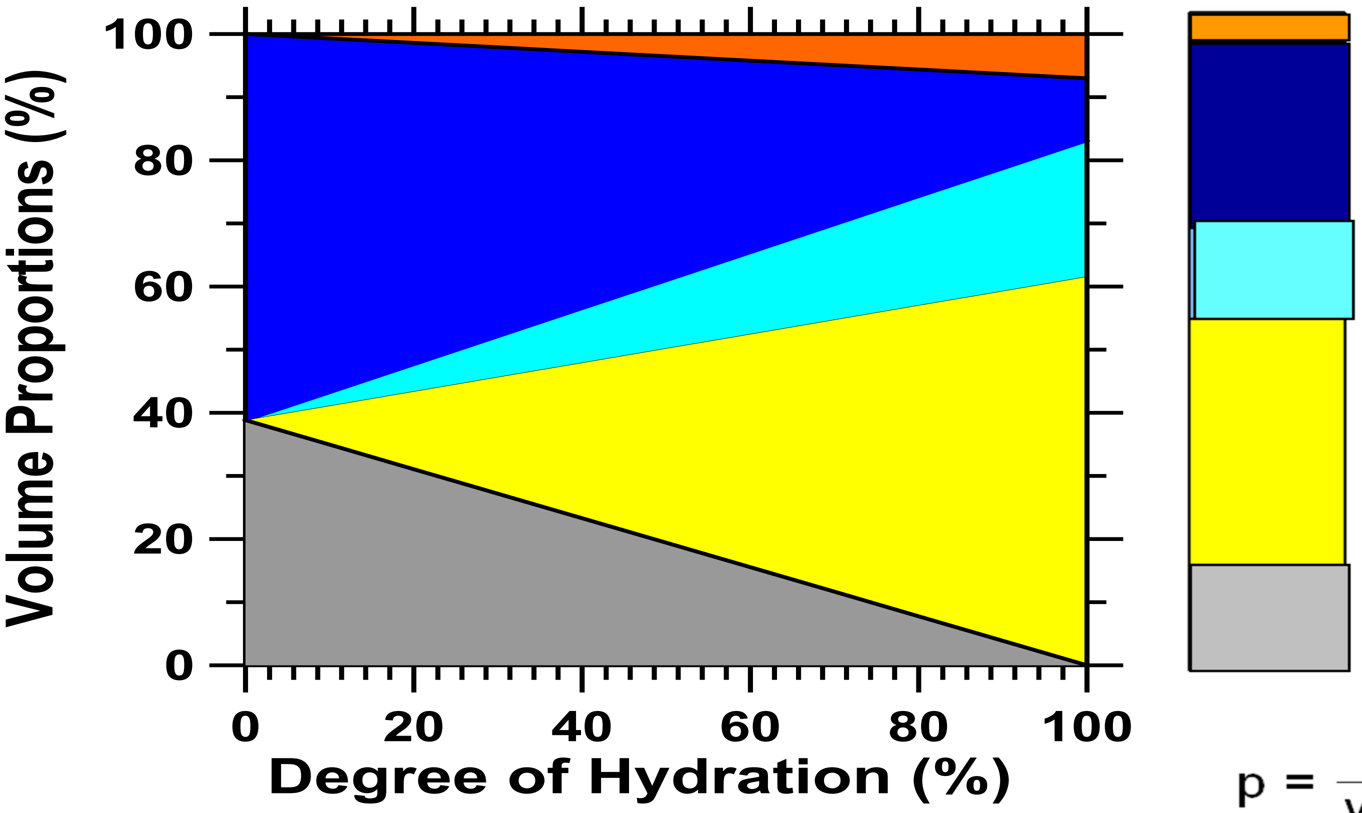
- Chemical Shrinkage
- Water
- Gel Water
- Gel Solid
- Cement



$V_{c.s} = 0.2\cdot(1-p)\cdot\alpha$

$V_{c.w} = p - 1.3\cdot(1-p)\cdot\alpha$

$V_{g.w} = 0.6\cdot(1-p)\cdot\alpha$

$V_{g.s} = 1.5\cdot(1-p)\cdot\alpha$

$V_{c} = (1-p)\cdot(1-\alpha)$

$$p = \frac{w/c}{w/c + \rho_w/\rho_c}$$

$\rho_c = 3150\ kg/m^3$

$\rho_w = 1000\ kg/m^3$

Water to Cement Ratio = 0.50

Thermodynamic Model

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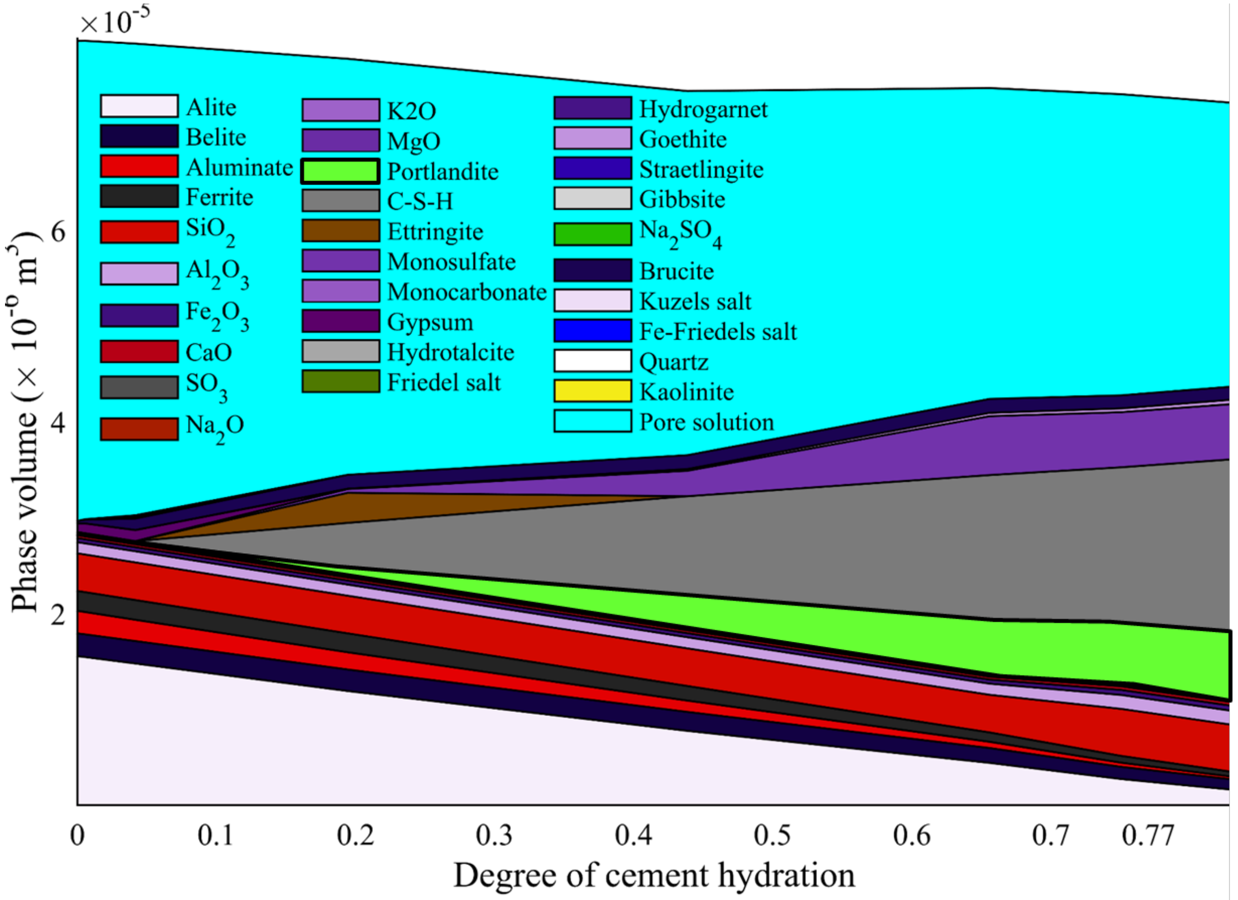
- PB – can do SCM/IBM
- Using GEMS to predict the reacted products
- 'How does this work'



Azad et al. 2016

It Must Be Magic

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Thermodynamics

- Set of well established rules
- Goal is to allow us to determine the reaction products that form if we know the initial constituents

- It's a bit like putting together a puzzle and figuring out where the pieces fit together the best

Thermodynamic modeling

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INPUT

1000 g OPC + 400 g H_2O →

$425\ g\ C_3S$
$325\ g\ C_2S$
$80\ g\ C_3A$
$70\ g\ C_4AF$

$30\ g\ Na_2O$
$20\ g\ K_2O$

50 g gypsum ($CaSO_4$)

What is the most thermodynamically feasible combination of products???

OUTPUT

??? g of C-S-H

C-S-H-1, C-S-H-2, etc.

??? g of CH

??? g of AFm

AFm1, AFm2, etc.

??? g of AFt

AFt1, AFt2, etc.

??? pore solution

Ca+2, Na+, K+, etc.

} 1,400 g

Thermodynamic modeling

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College of Engineering

INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
20 g K_2O

50 g gypsum ($CaSO_4$)

Gibbs Free Energy

OUTPUT 1

500 g of C-S-H

C-S-H-1, C-S-H-2, etc.

400 g of CH

200 g of AFm

AFm1, AFm2, etc.

200 g of AFt

AFt1, AFt2, etc.

100 g pore solution

Ca+2, Na+, K+, etc.

1,400 g

Thermodynamic modeling

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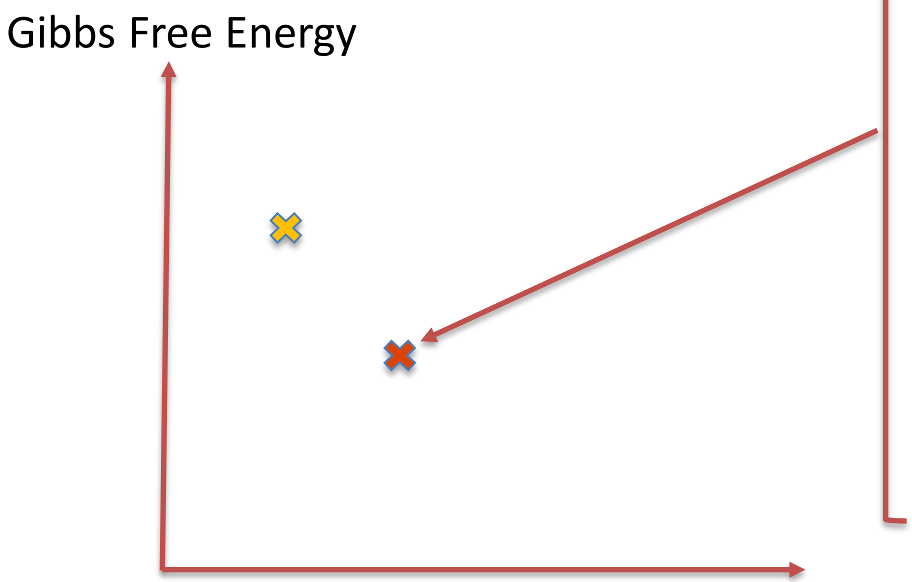
INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
20 g K_2O

50 g gypsum ($CaSO_4$)



OUTPUT 2

550 g of C-S-H
C-S-H-1, C-S-H-2, etc.

350 g of CH

175 g of AFm
AFm1, AFm2, etc.

225 g of AFt
AFt1, AFt2, etc.

100 g pore solution
Ca+2, Na+, K+, etc.

1,400 g

Thermodynamic modeling

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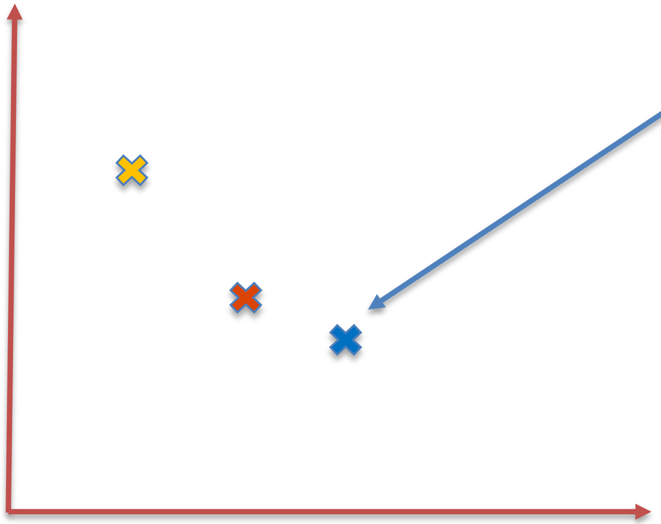
INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
20 g K_2O

50 g gypsum ($CaSO_4$)



OUTPUT n

555 g of C-S-H
C-S-H-1, C-S-H-2, etc.
345 g of CH
180 g of AFm
AFm1, AFm2, etc.
210 g of AFt
AFt1, AFt2, etc.
110 g pore solution
Ca+2, Na+, K+, etc.

1,400 g

Thermodynamic modeling

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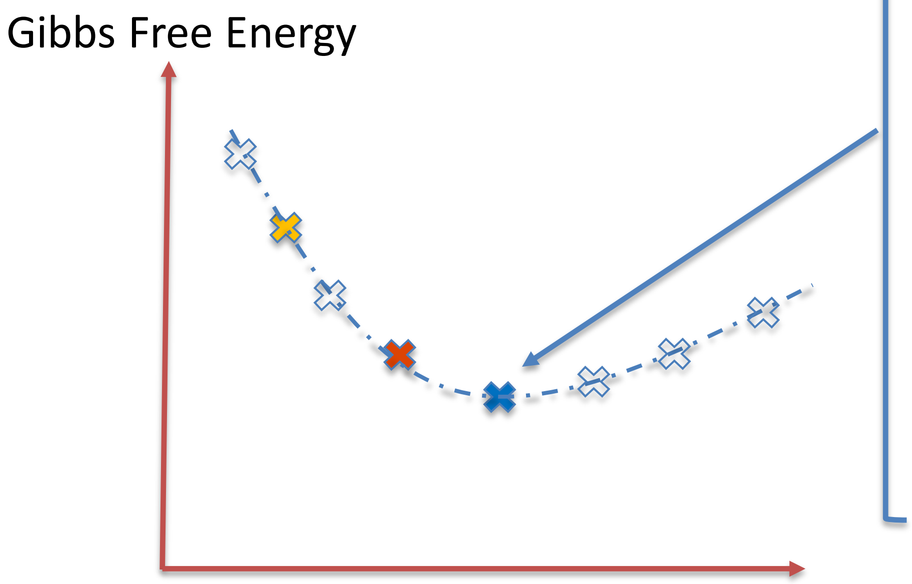
INPUT

1000 g OPC + 400 g H_2O

425 g C_3S
325 g C_2S
80 g C_3A
70 g C_4AF

30 g Na_2O
20 g K_2O

50 g gypsum ($CaSO_4$)



GEMS

SOLUTION

555 g of C-S-H

C-S-H-1, C-S-H-2, etc.

345 g of CH

180 g of AFm

AFm1, AFm2, etc.

210 g of AFt

AFt1, AFt2, etc.

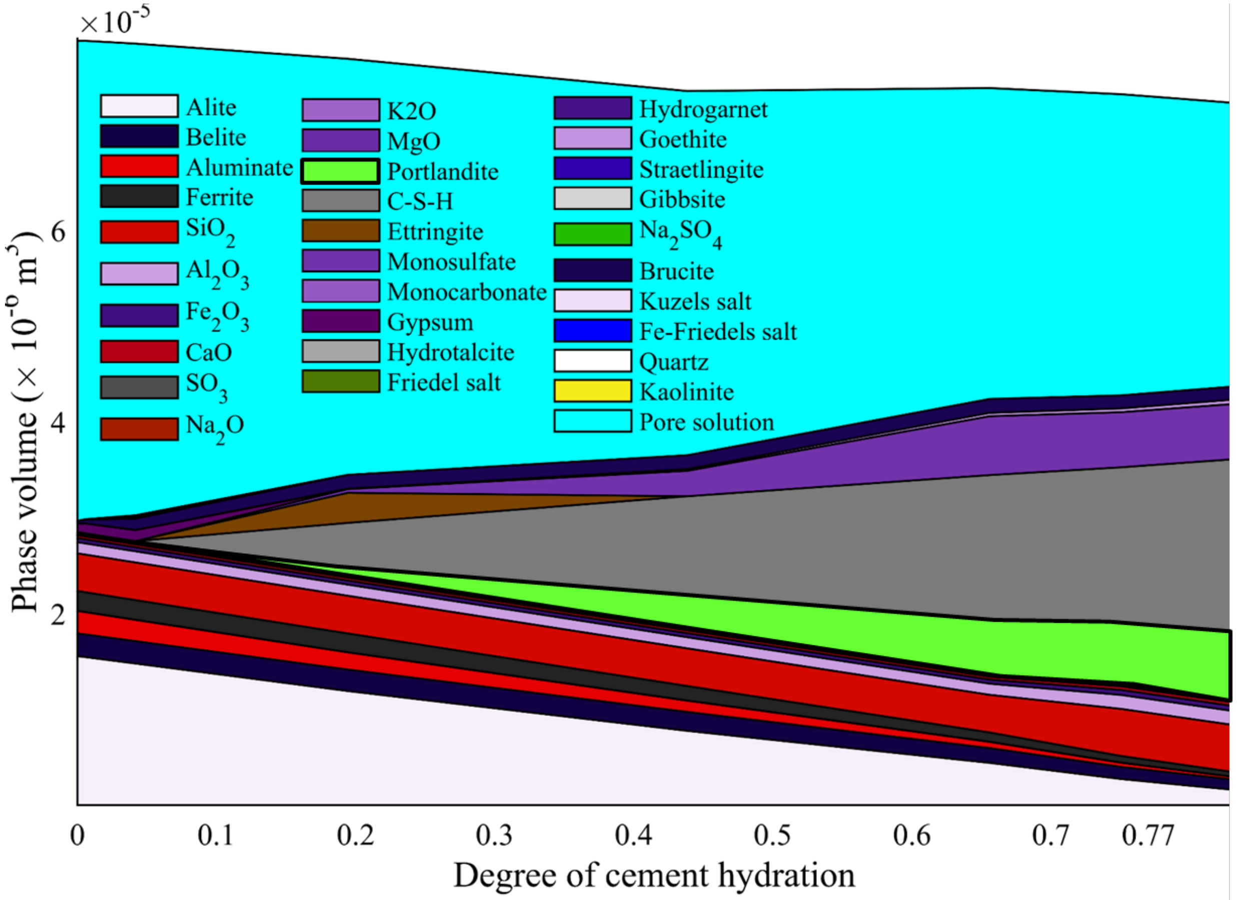
110 g pore solution

Ca+2, Na+, K+, etc.

1,400 g

Thermodynamic Model

- Using GEMS to predict the reacted products
- Provides volumes but does not segment pores



Azad et al. 2016

The Porosity Plot 2.0

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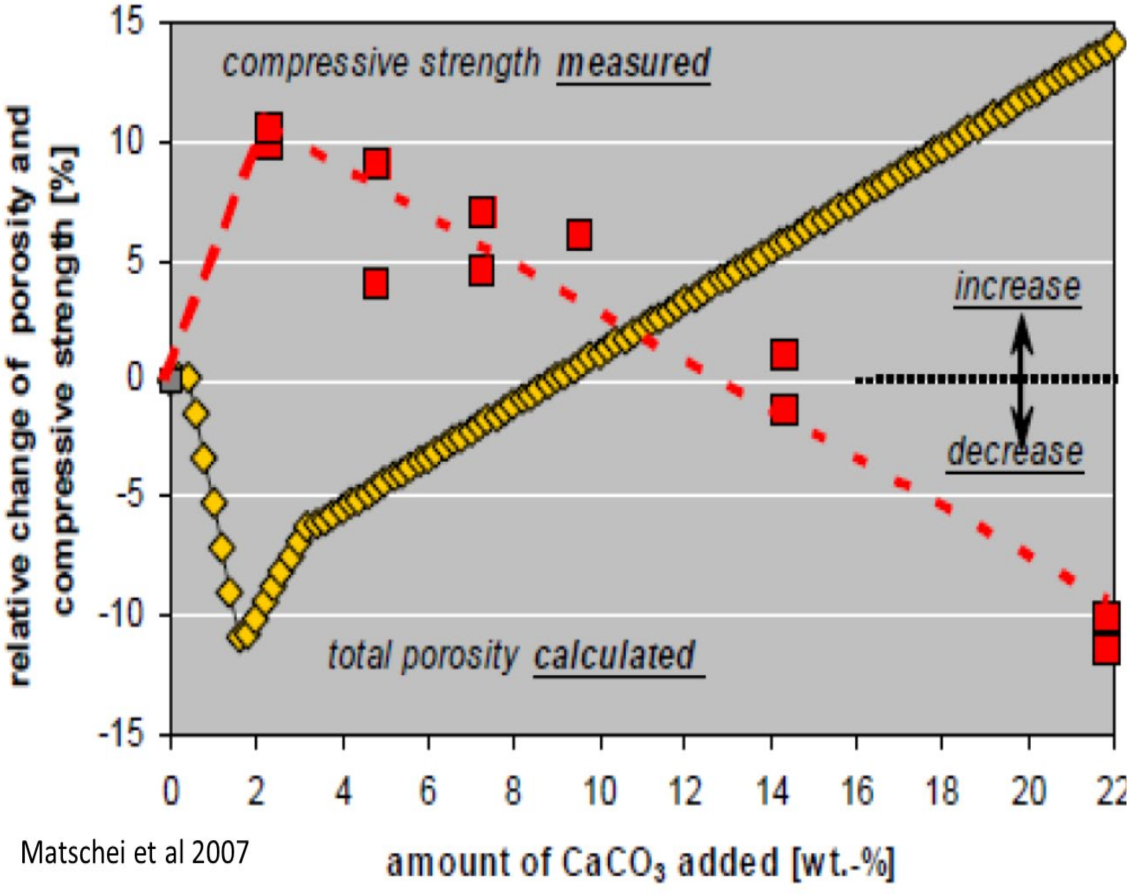
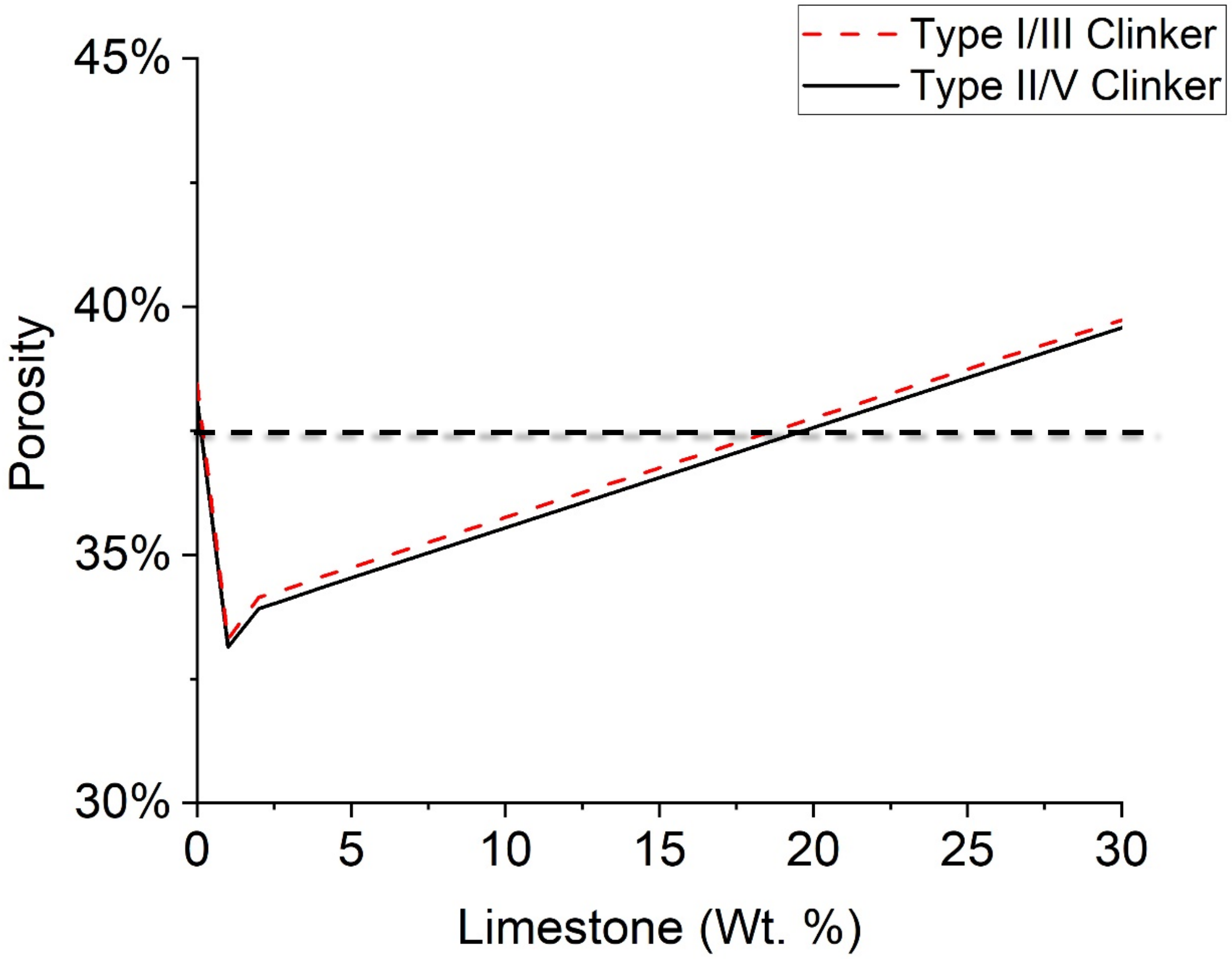
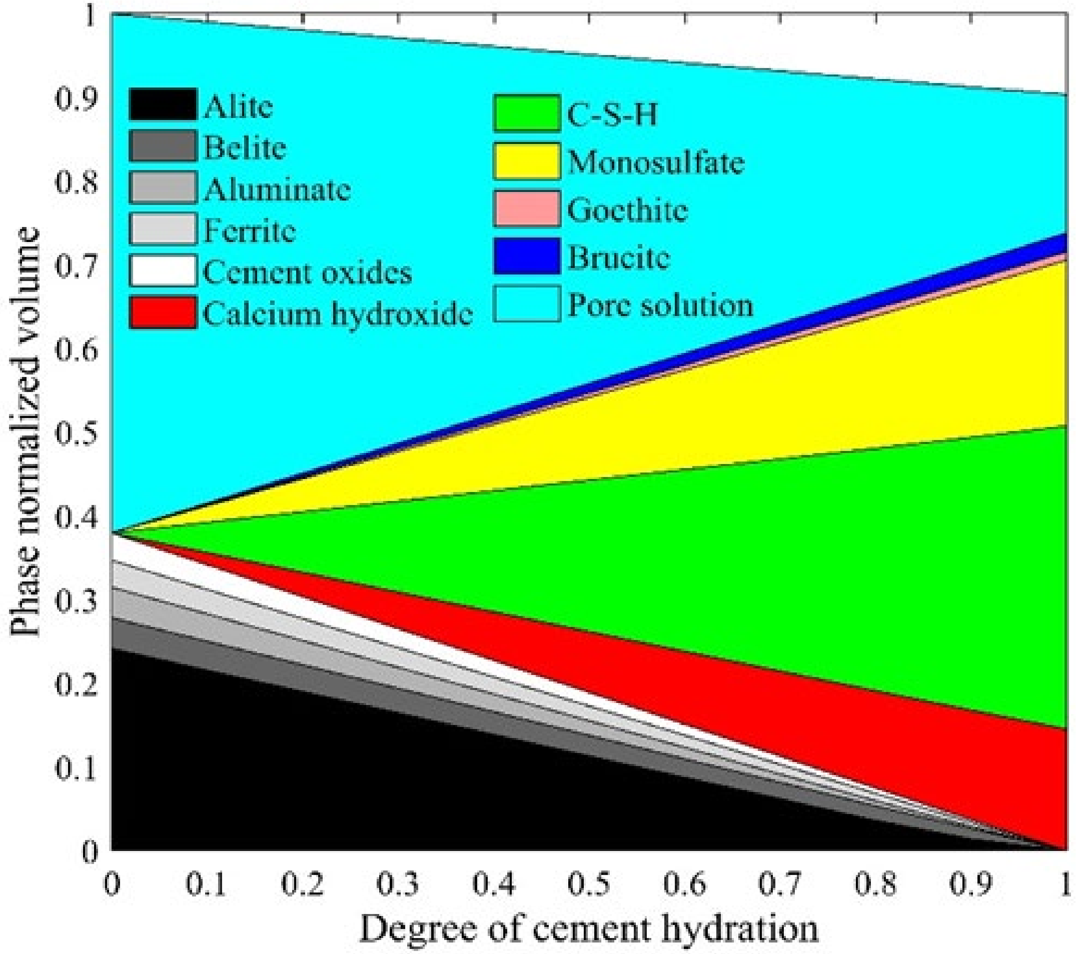
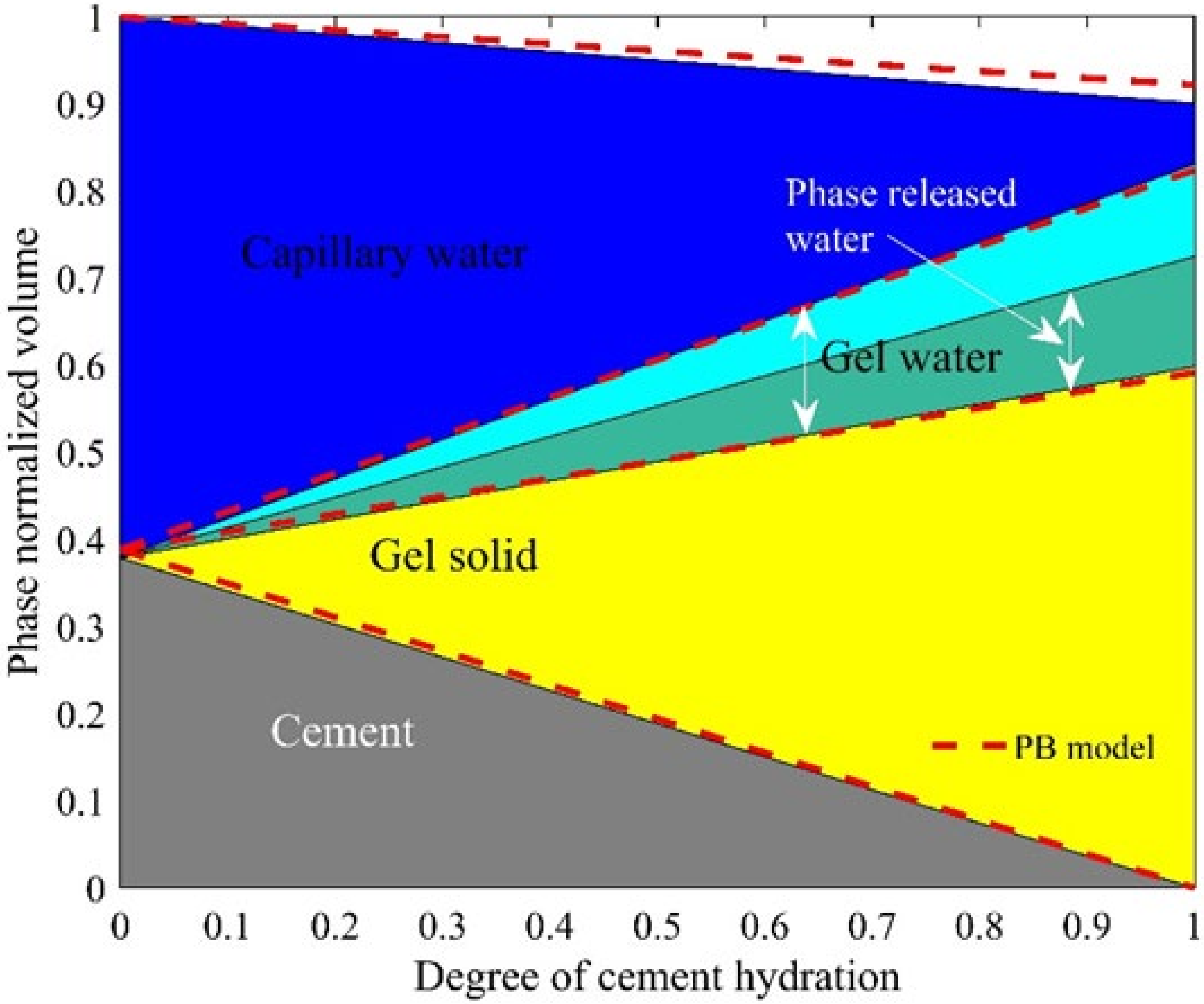


Matschei et al 2007



Powers to GEMS





Modeling framework

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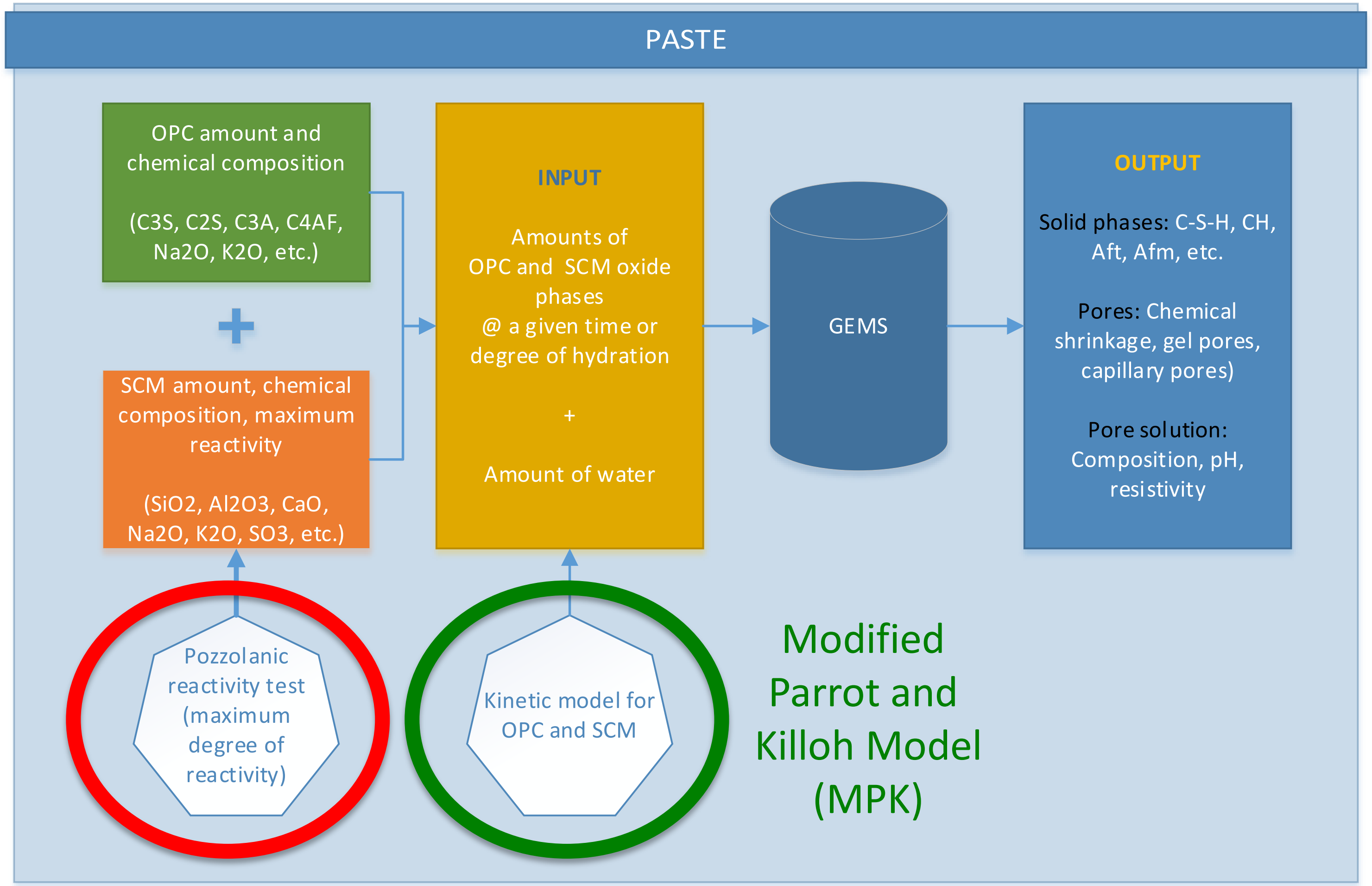

Pozzolanic Reactivity Test (PRT)

Modeling framework

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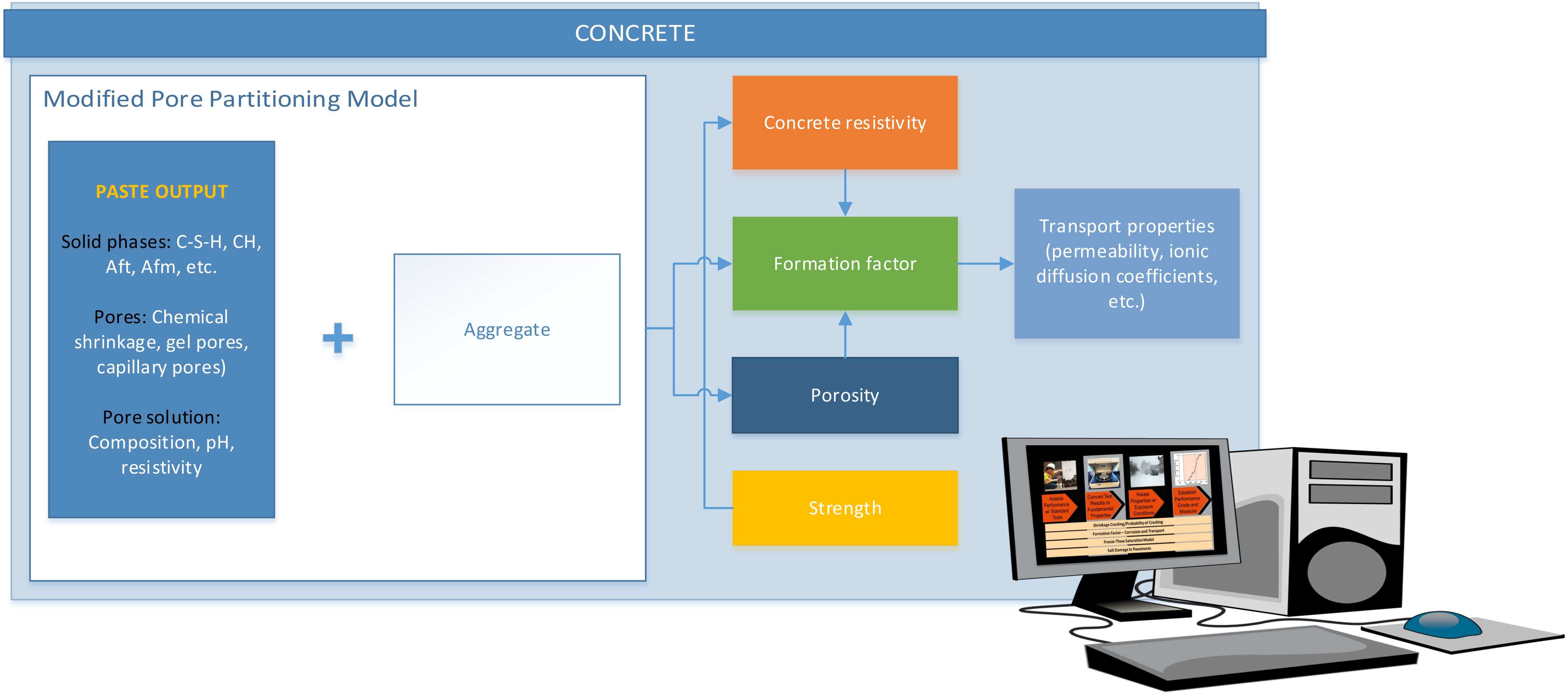

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Question #1: Type I/III vs. Type II/V clinker

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a) What is the impact of replacing clinker with limestone?

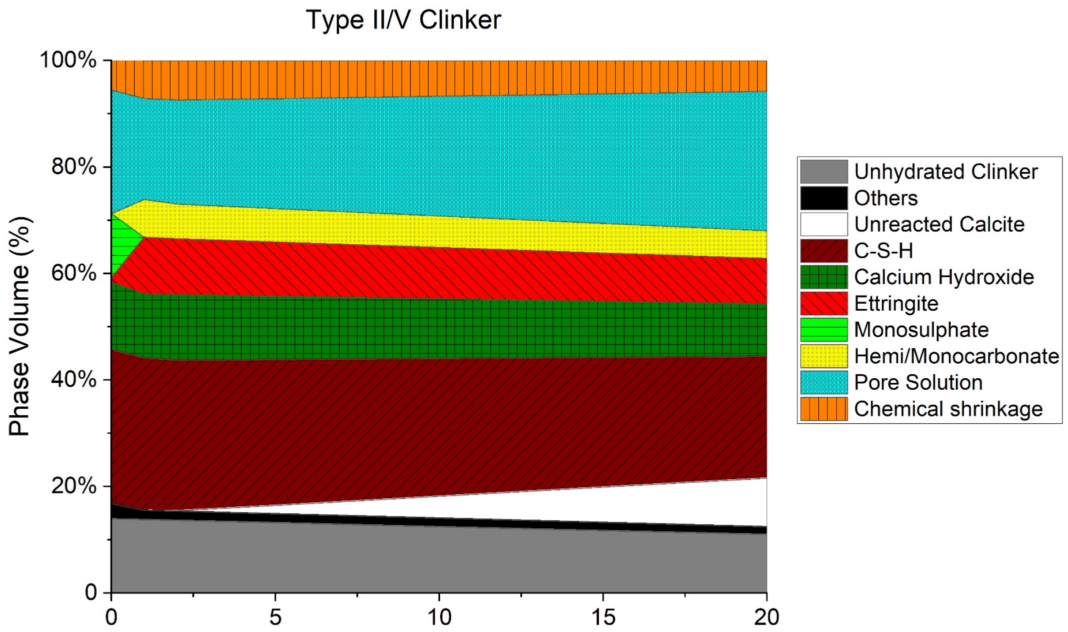
b) What is the difference in chemical composition and porosity when we use Type I/III and Type II/V clinkers?

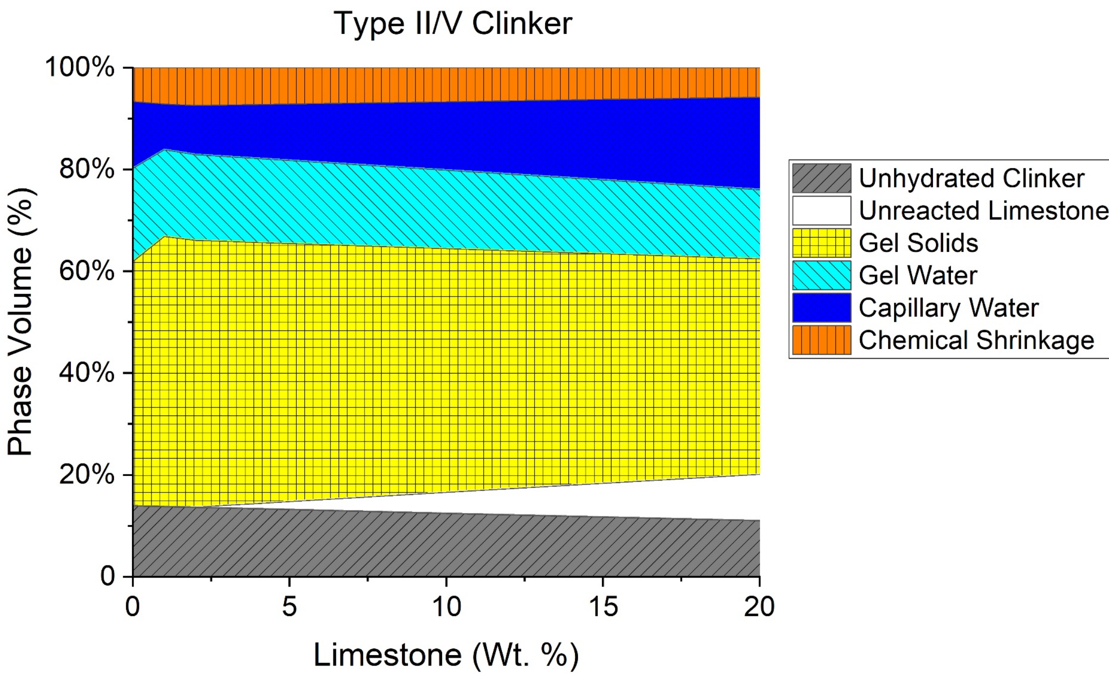
What does Limestone do to phase assemblage

Limestone changes the phase assemblage of OPC systems:

- Ettringite and hemi/monocarbonate phases form instead of monosulfate
- Slightly lower calcium hydroxide (~1-2g lower)

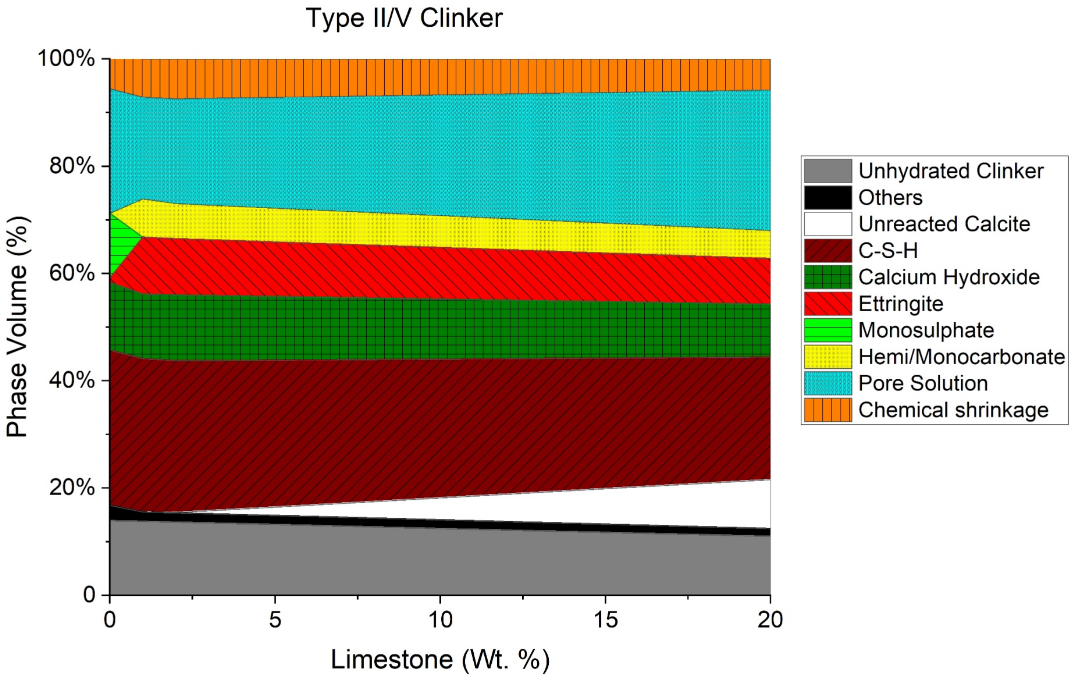
The porosity decreases rapidly as Ls increases from 0% to 2% (due to formation of space filling ettringite and carboaluminates)

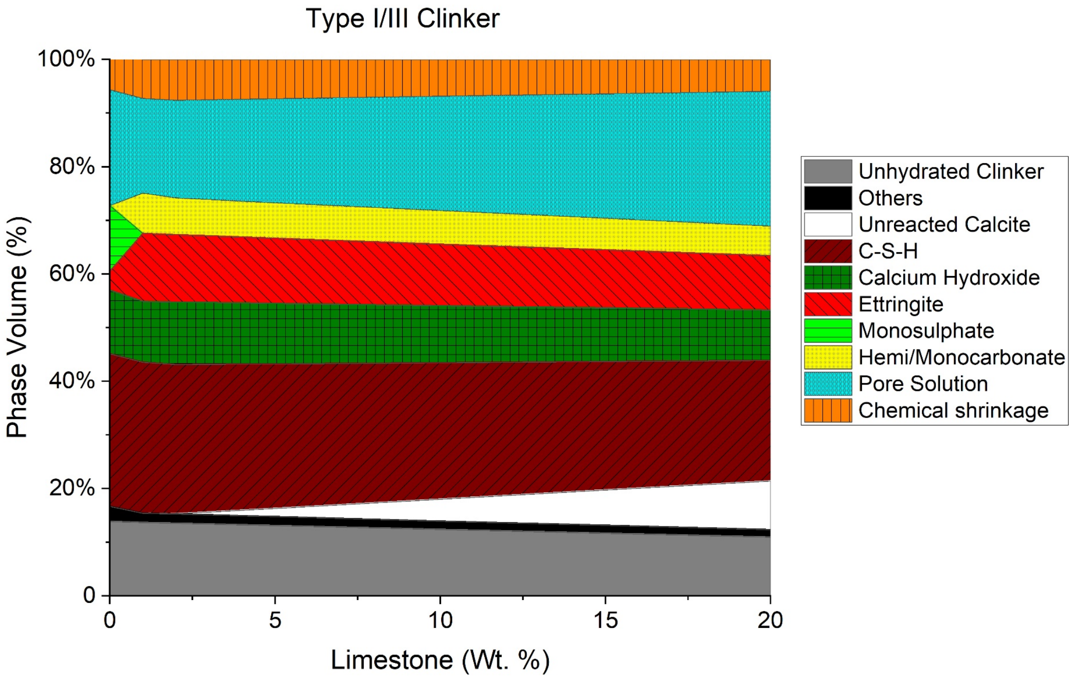




Type I/III vs. II/V: Phase Formations

- Type II/V clinkers have slightly lower alumina than Type I/III
- Clinker with lesser alumina can react less with limestone, so lesser ettringite + carboaluminates form





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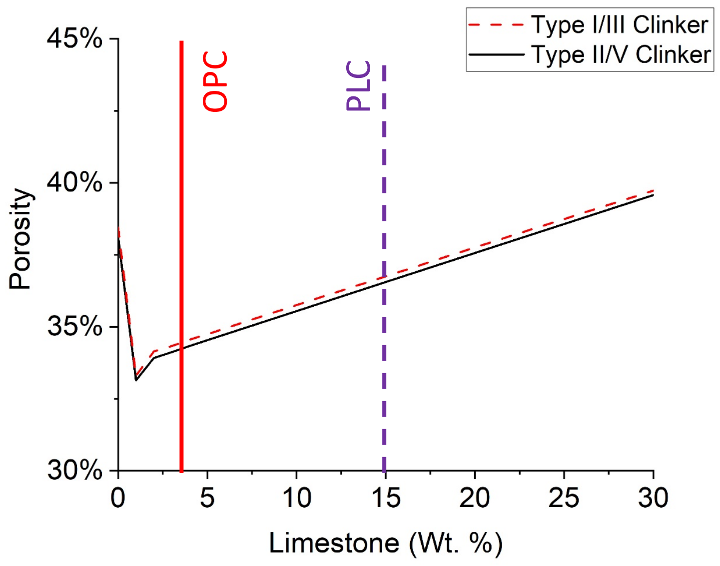
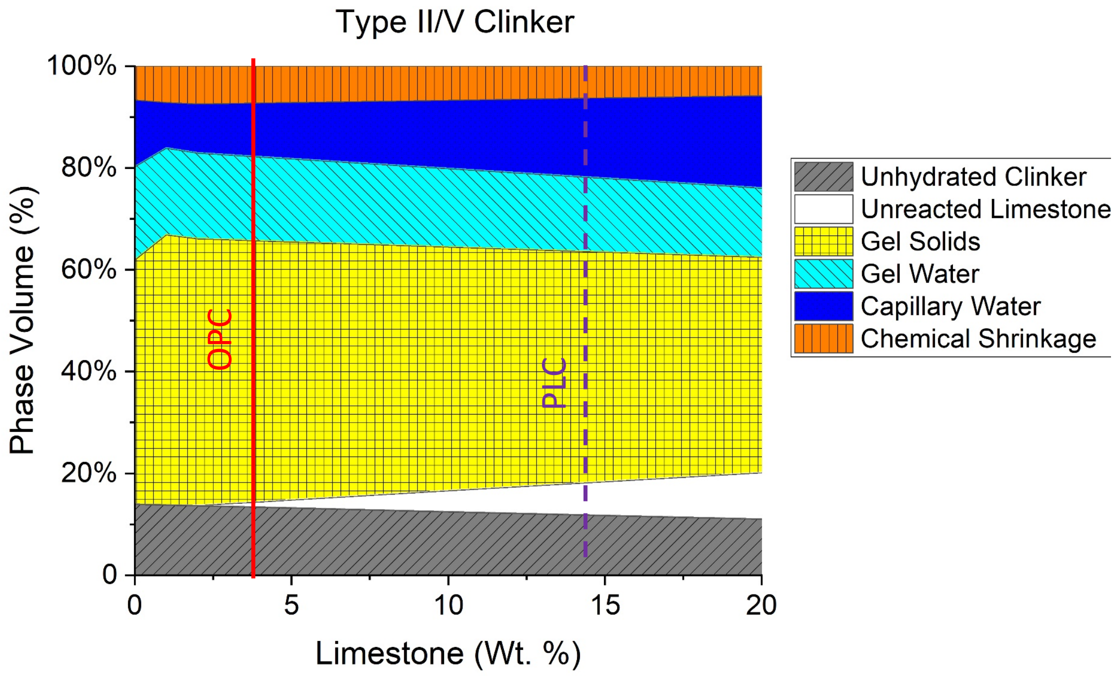
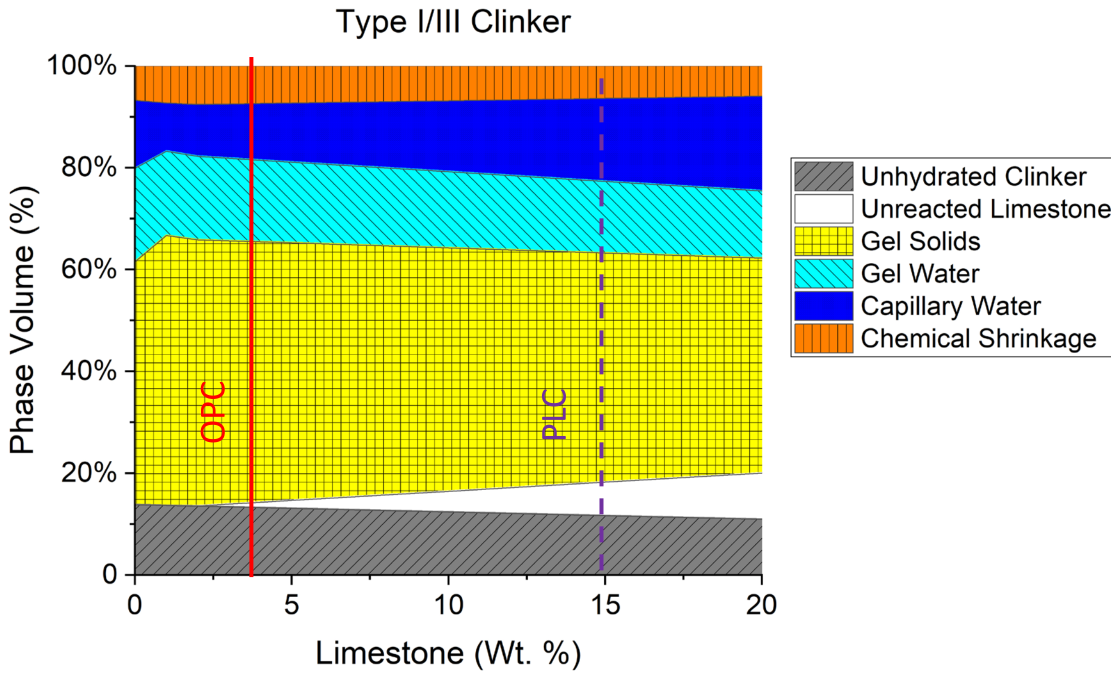
Impact of Limestone on Performance of PLC

- The porosity decreases rapidly as Ls increases from 0% to 2% (due to formation of space filling ettringite and carboaluminates)
- Any further limestone causes dilution which increases porosity



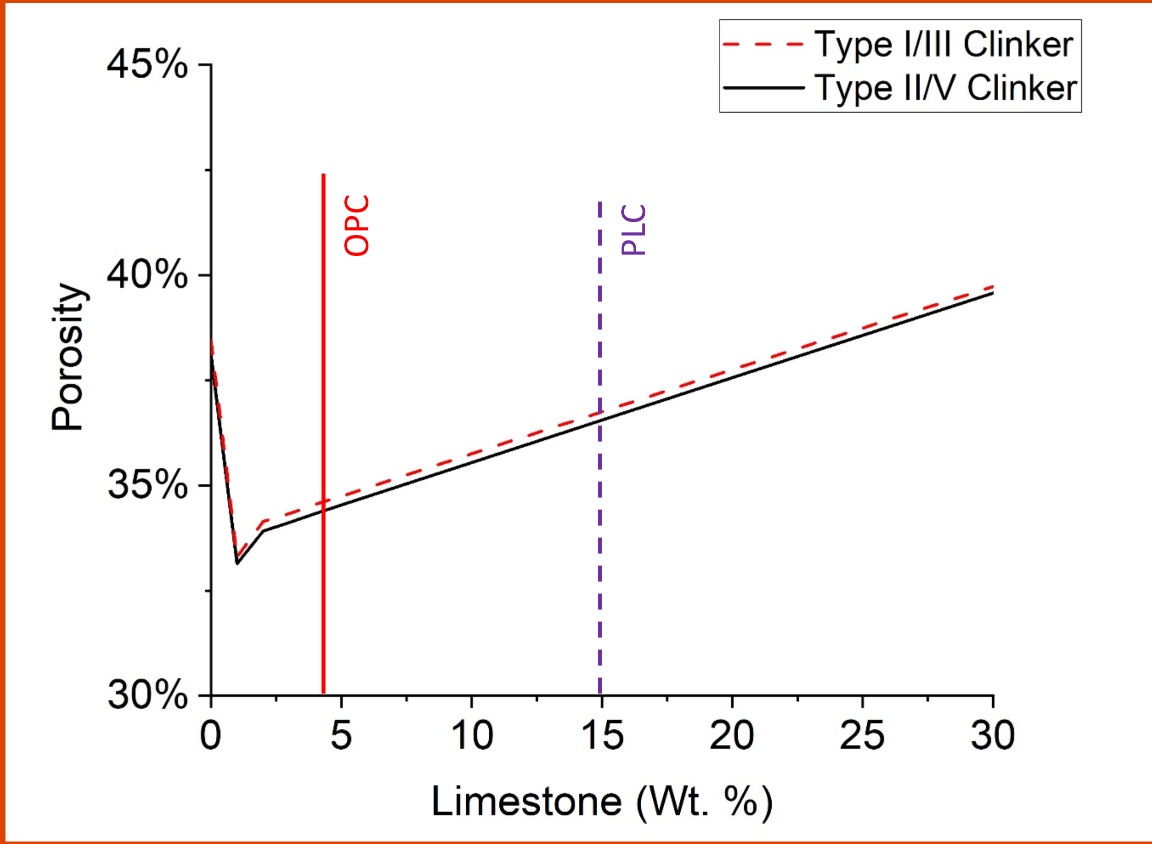




Takeaway #1

a) The porosity decreases rapidly as Ls increases from 0% to 2%; any further limestone addition causes an increase in porosity

b) The porosity is not that different between Type I/III and II/V clinkers (<1% difference)



Question #2: PLC+SiO_2 and PLC+Al_2O_3 systems

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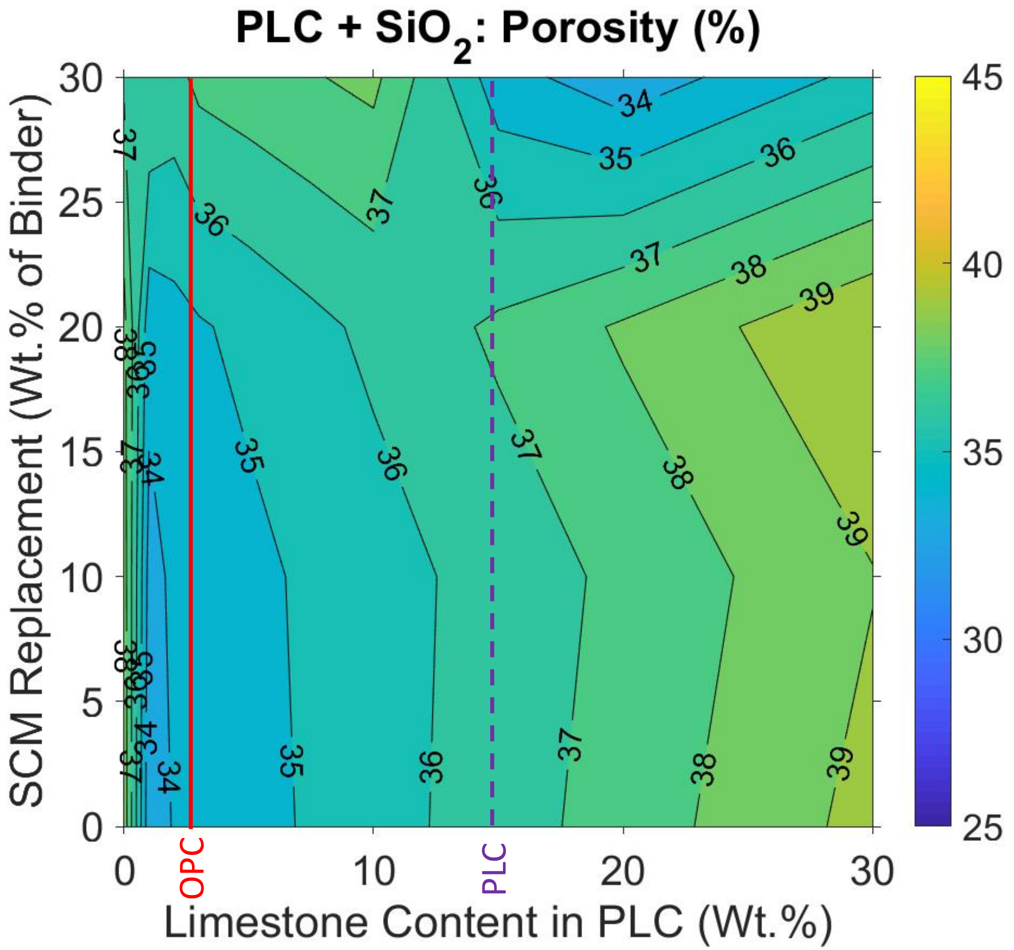
What happens when we add pure oxides or “ideal SCMs” (SiO_2 and Al_2O_3) to PLC systems?

PLC + SCM (SiO_2)

- Silica reacts with CH to form more C-S-H with a lower C/S:
  - Same porosity but a highly refined microstructure
- Silica does not react with carbonates (from limestone) and as such the Ls content of PLC has little impact on the reaction products of PLC+SF systems
  - Minimum porosity is at 2% Ls



PLC + SCM (Al_2O_3)

- Alumina can react with calcium carbonate in the limestone to form hemicarbonate and monocarbonate:
  - $A + CH + H + Cc \rightarrow C_3A \cdot (CH)_{0.5}(Cc)_{0.5} \cdot H$ (Hemicarbonate)
  - $A + CH + H + Cc \rightarrow C_3A \cdot (Cc)_{0.5} \cdot H$ (Monocarbonate)
- Theoretically, 100g alumina can react with between 50-100g $CaCO_3$ to form Hc+Mc

PLC + Al_2O_3

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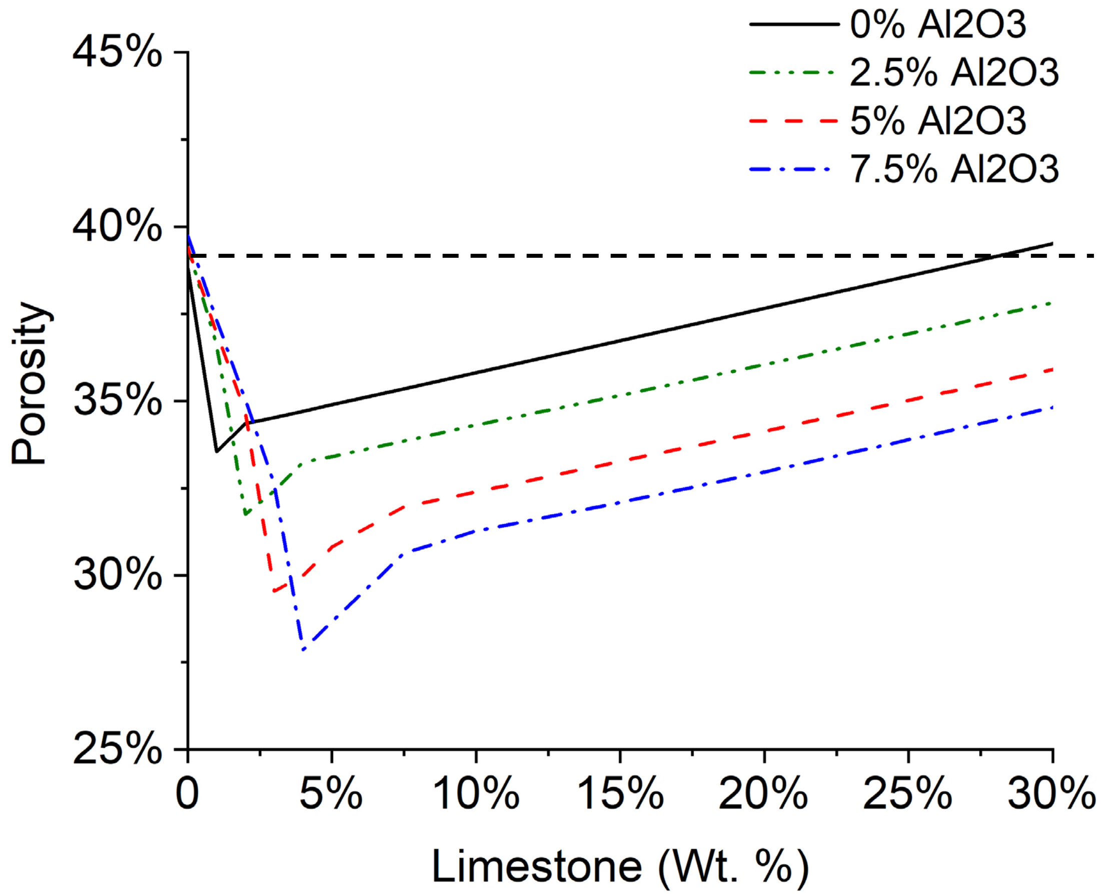
Alumina lowers porosity in PLC systems by:

1) reacting with CH & C-S-H to form C-(A)-S-H: slightly Lowers porosity and refines microstructure
2) reacting with carbonates when CH is present to form carboaluminates which fills space and decrease porosity



PLC + Al_2O_3

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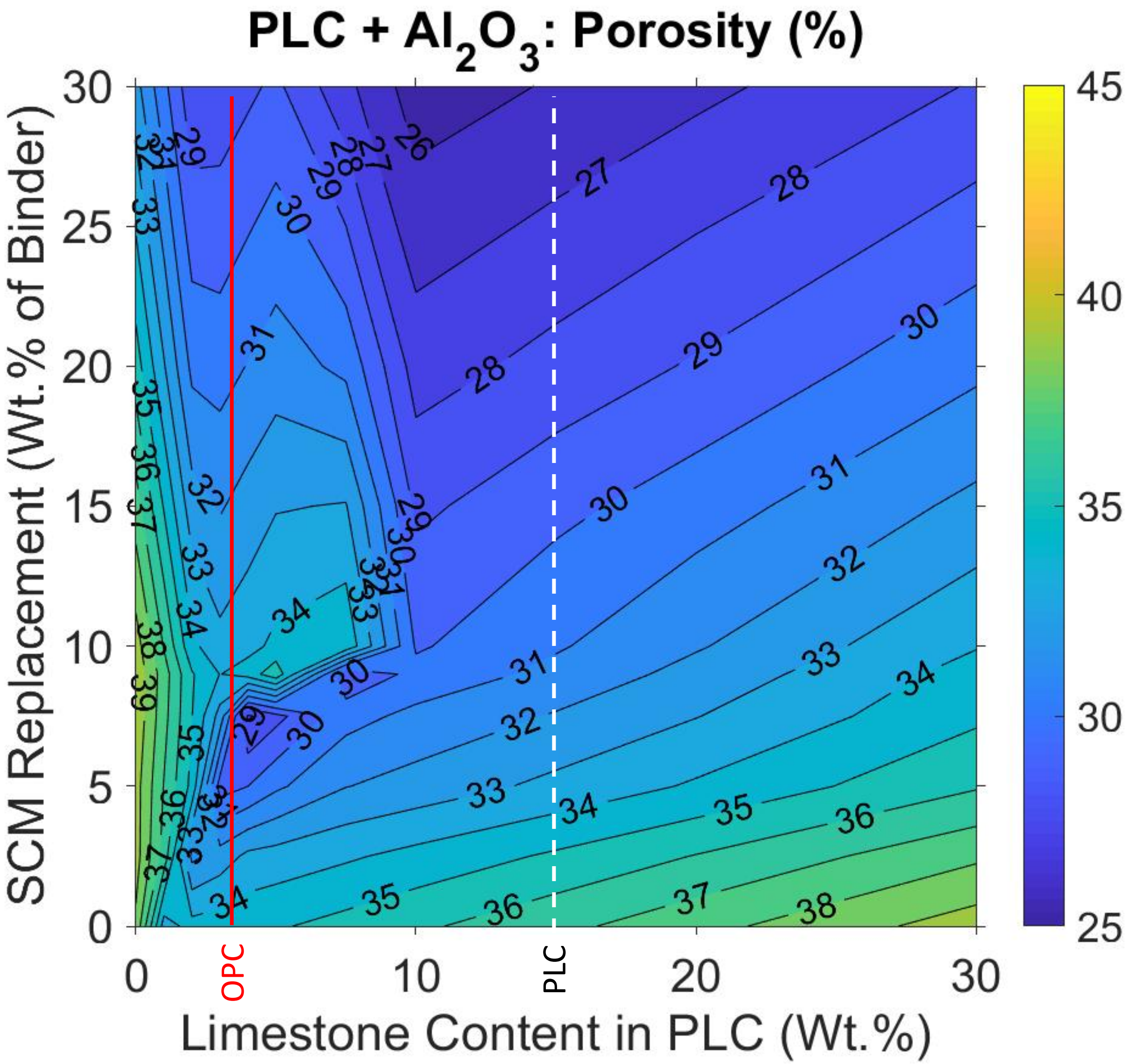
- Up to 10% Al_2O_3, limestone reacts with Al_2O_3 to form carboaluminates
- Above 10% Al_2O_3, all CH is consumed so C-(A)-S-H phases form instead of Hc/Mc (porosity decrease)
- Any further limestone causes dilution (porosity increase)



pH of Solution

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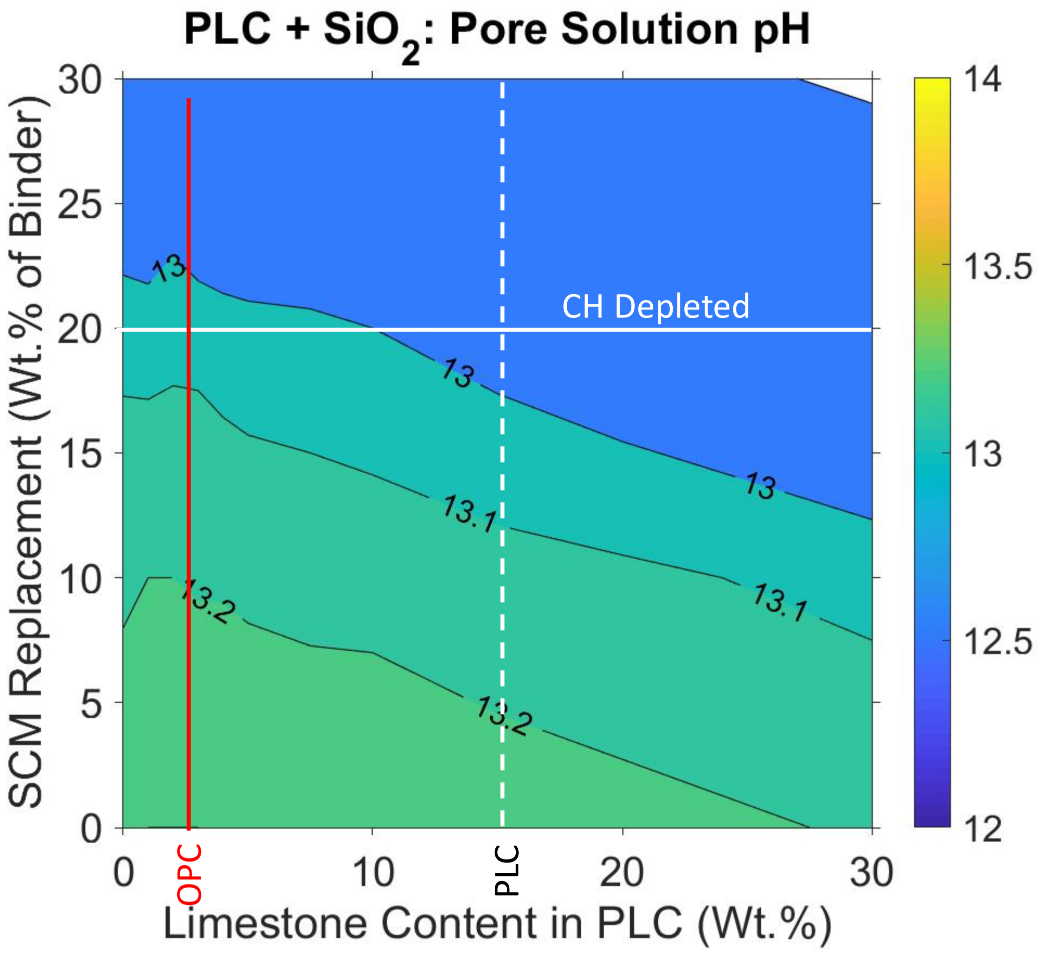
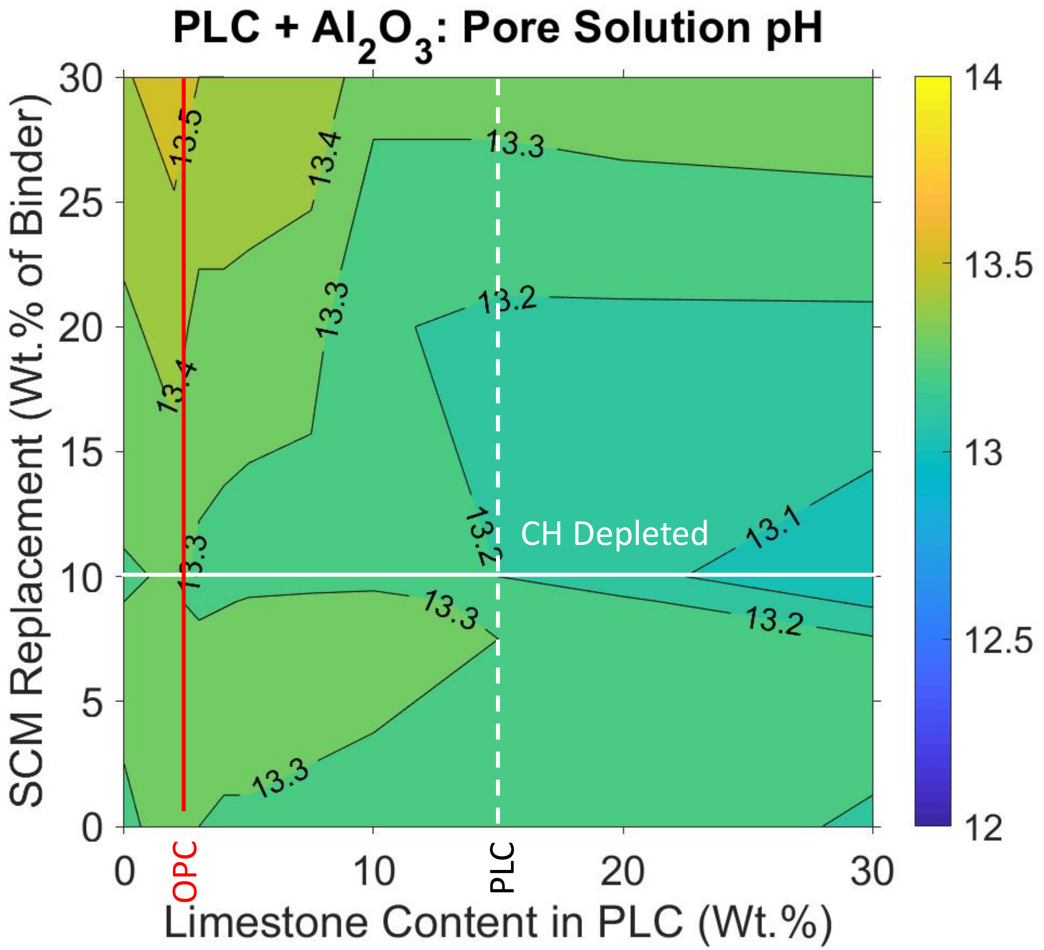
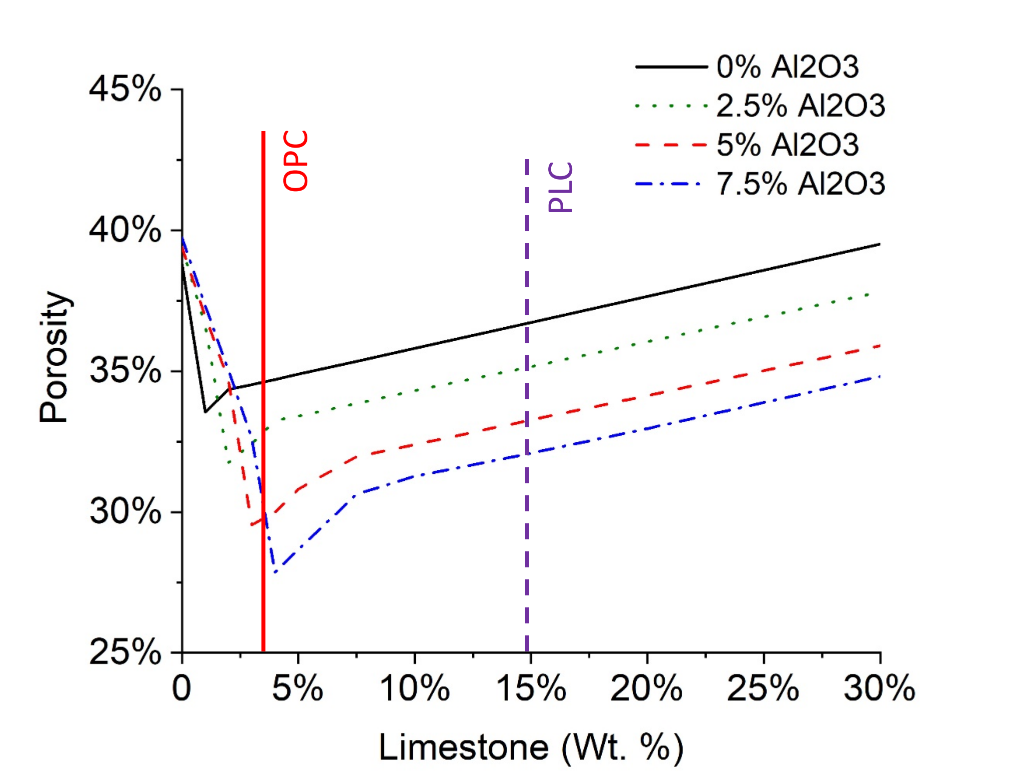




Takeaway #2

a) Silica doesn't react with limestone and has minimal impact on phases and porosity

b) Alumina does react with limestone to form carboaluminates and lowers porosity



Question #3: Performance of PLC+Slag

What happens when we add commercially available Slag to PLC systems?

PLC + Slag (SL)

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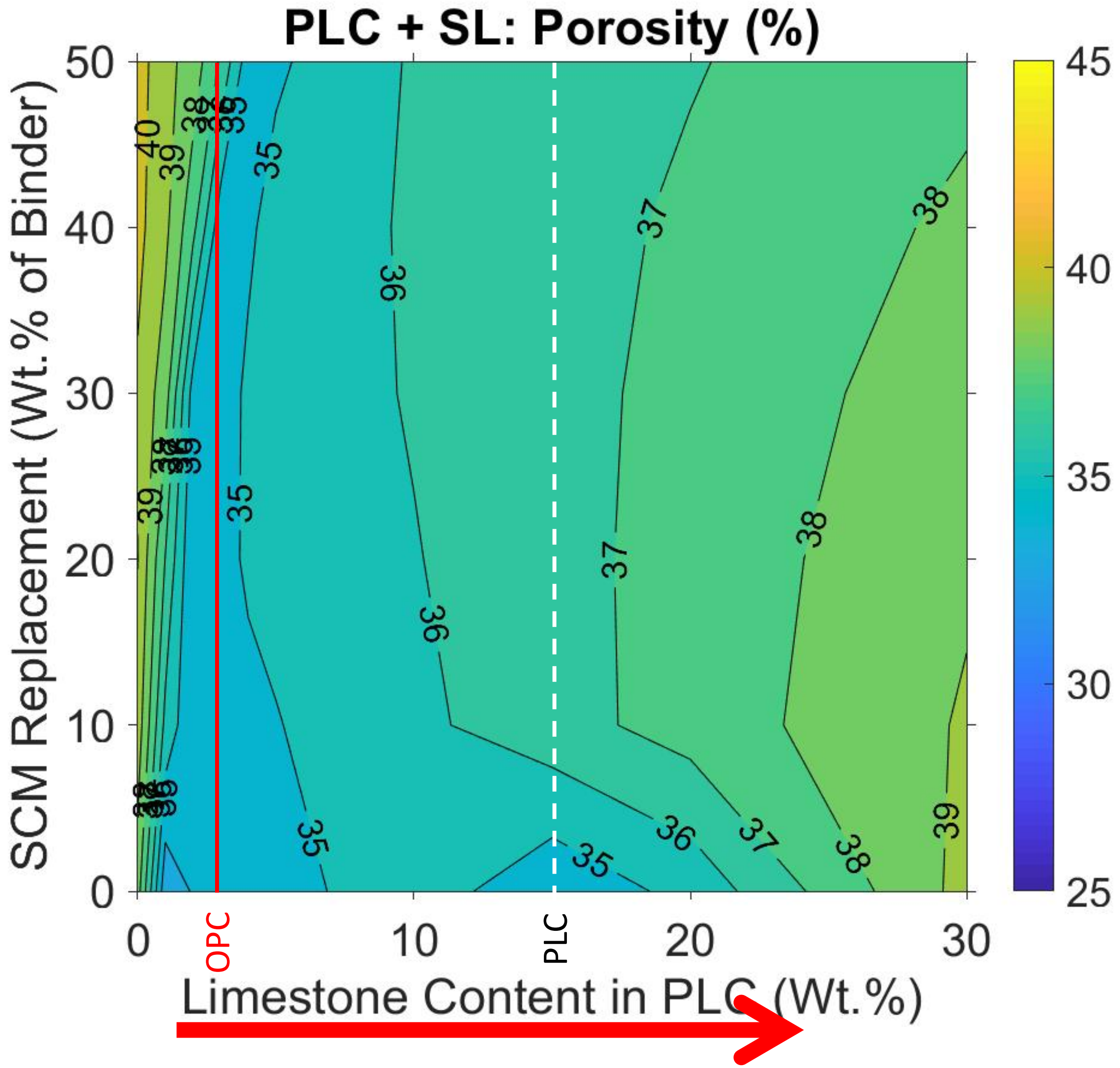
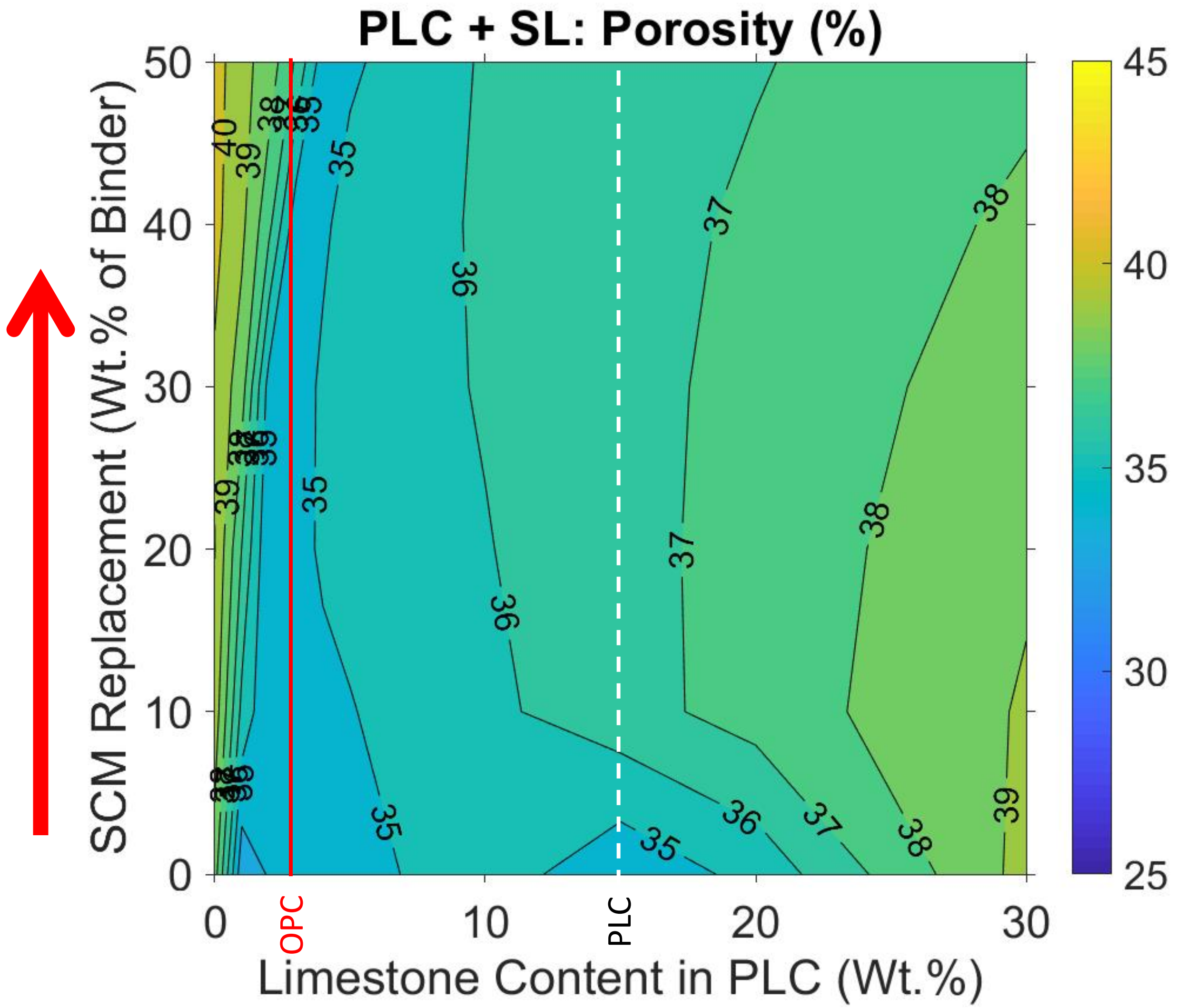
- SL contains ~35% silica, ~10% alumina, 40% CaO and has a reactivity of 60%
- SL reacts:
  – Pozzolanically to form C-(A)-S-H
  – Hydraulically to form CH
  – with limestone to form Hc+Mc
- As Ls increases, porosity decreases and then increases



PLC + Slag (SL)

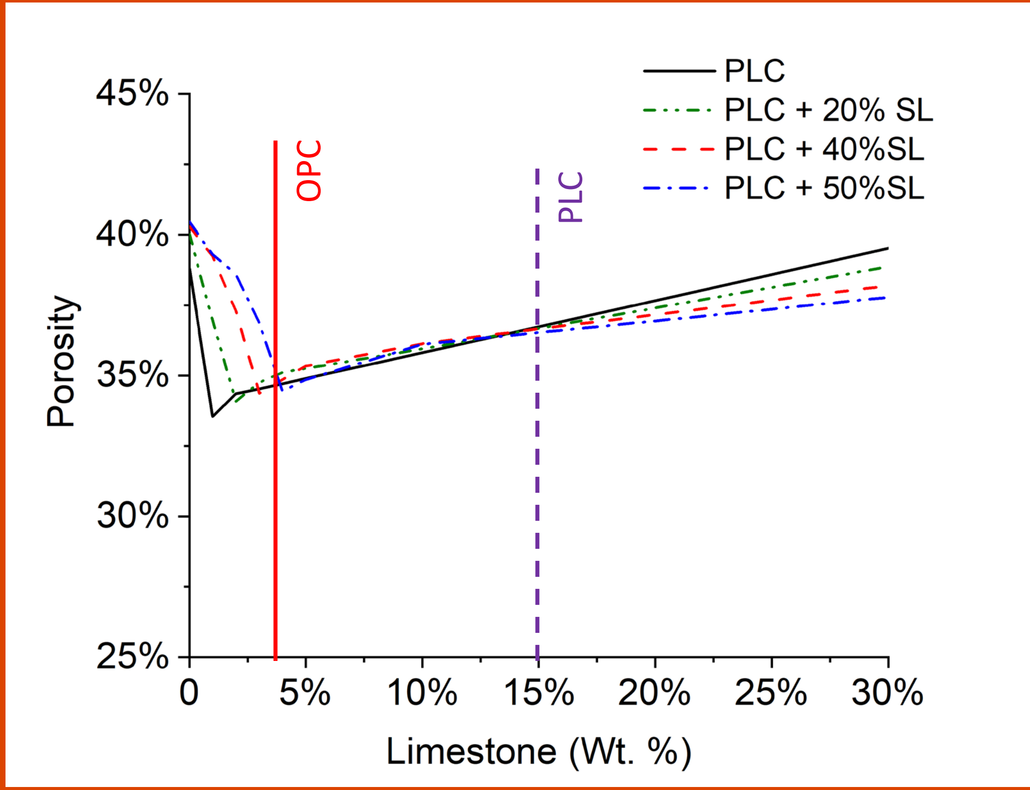
- Addition of slag doesn't significantly affect porosity
  - Hydraulic and pozzolanic reactions compensate dilution



Takeaway #3

SCMs like slag work to improve performance:

- PLC+SL: adding SL does not have a significant impact on the porosity



Objective #4: Experimental Results

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- Study the experimental results with the knowledge from modeling exercises

- Study the impact of direct replacement of OPCs with PLCs on the experimental mixtures

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More Alumina More Benefit

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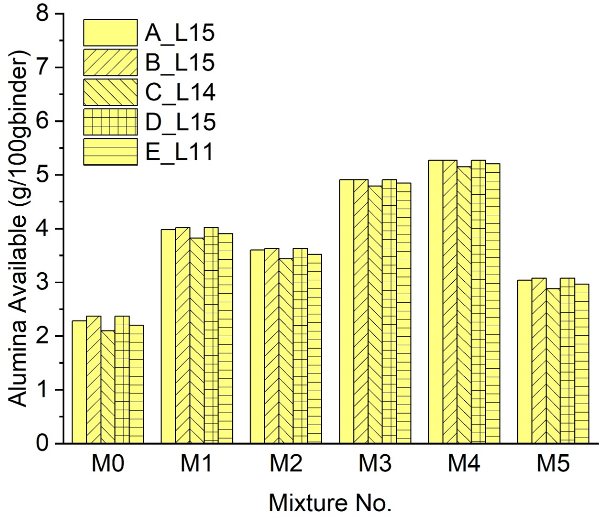
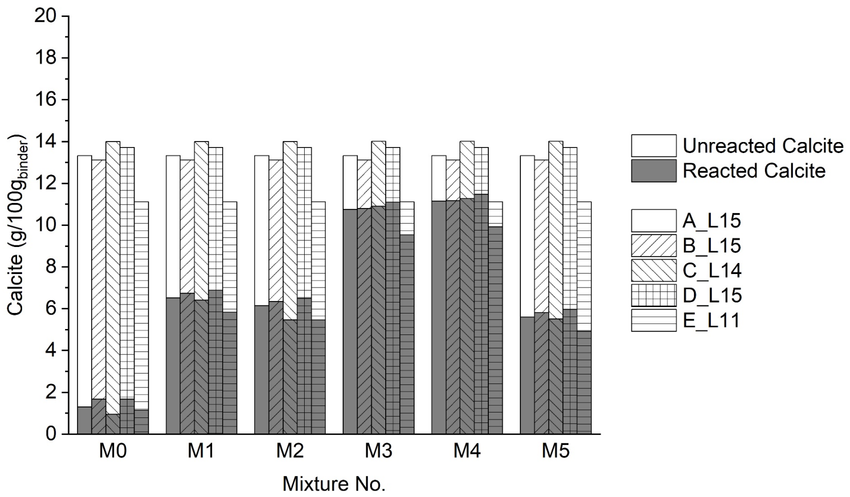
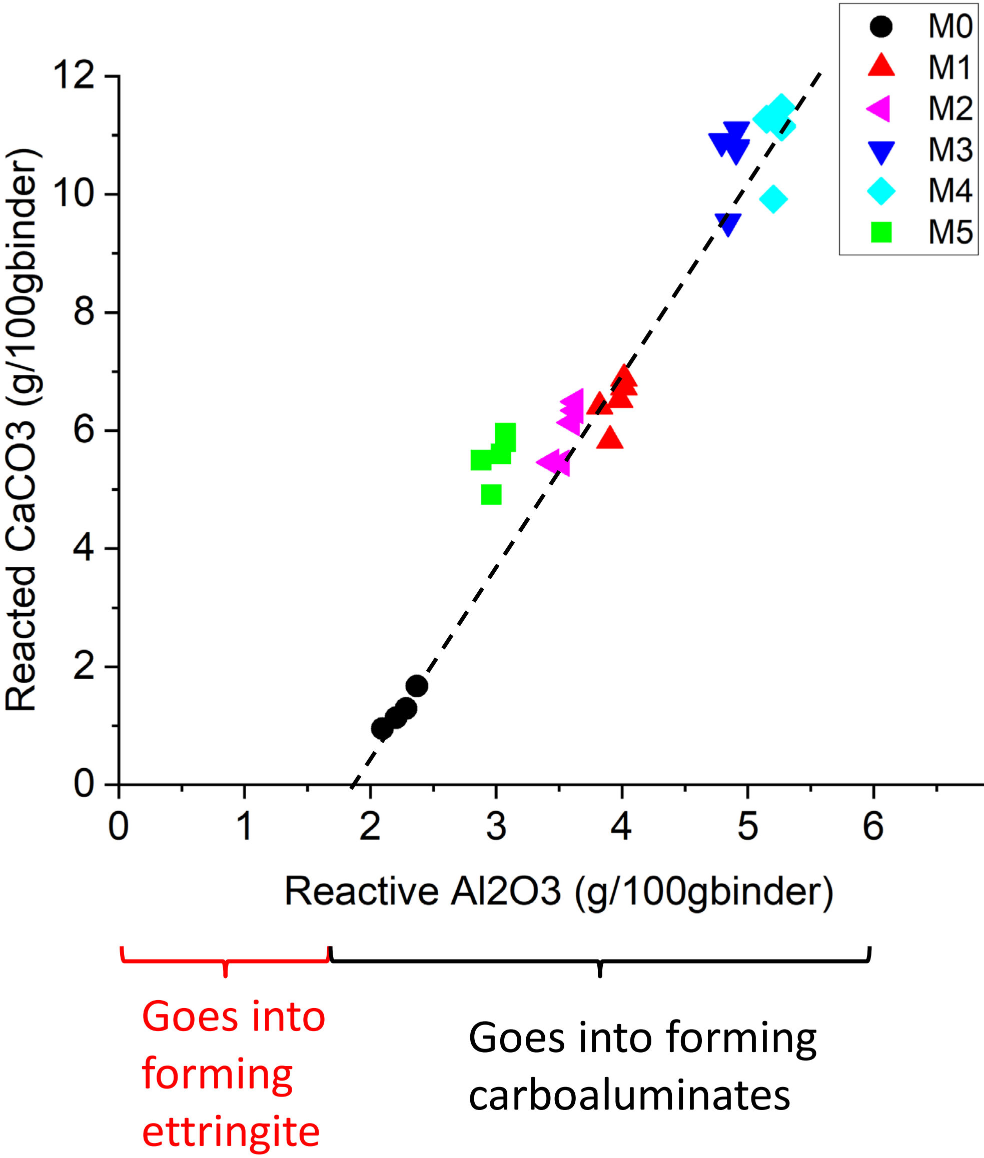


M0 = Control (OPC / PLC)
M1 = PLC + 25% FA
M2 = PLC + 20% FA + 5% SF
M3 = PLC + 50% Slag
M4 = PLC + 25% Slag + 25% FA
M5 = PLC + 25% NP





Porosity (Model vs. Exp)

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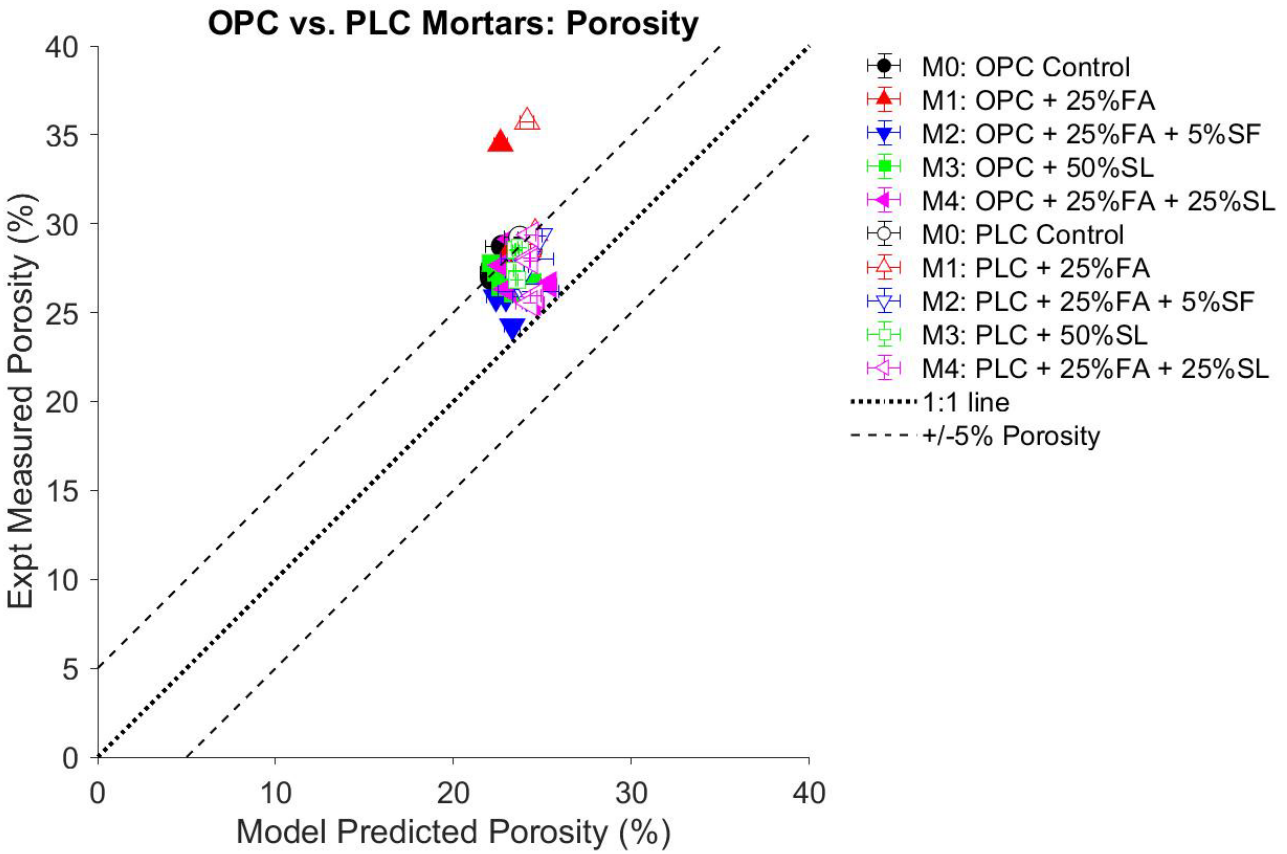
- The porosity is higher experimentally as we do not capture entrapped air into the system (assuming 2 to 3 % puts it in target)

- One exception is one mixture of M1 with higher measured porosity



OPC vs. PLC Model: CH Consumed

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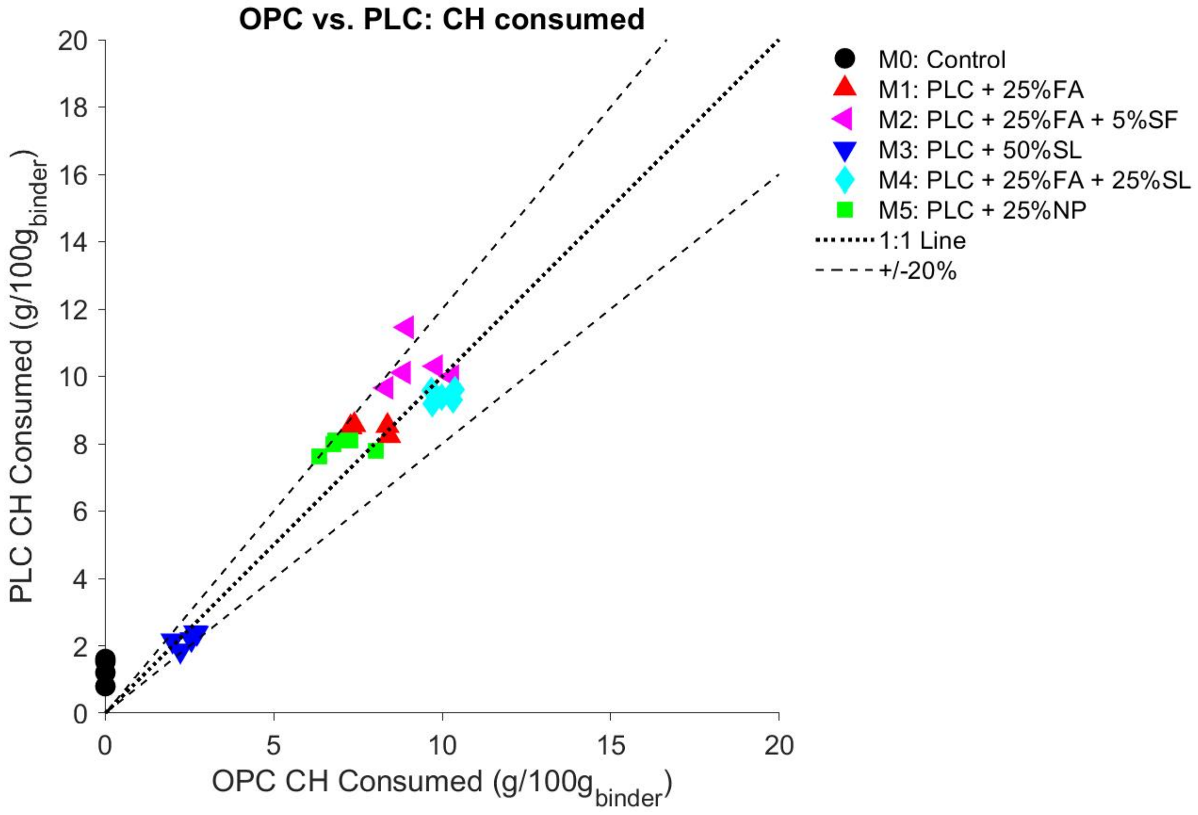
- Direct replacement of OPC with PLC increases CH consumed due to carboaluminate reactions

- Carboaluminate reactions that consume CH can also cause pore refinement



OPC vs. PLC Model: Phases that form

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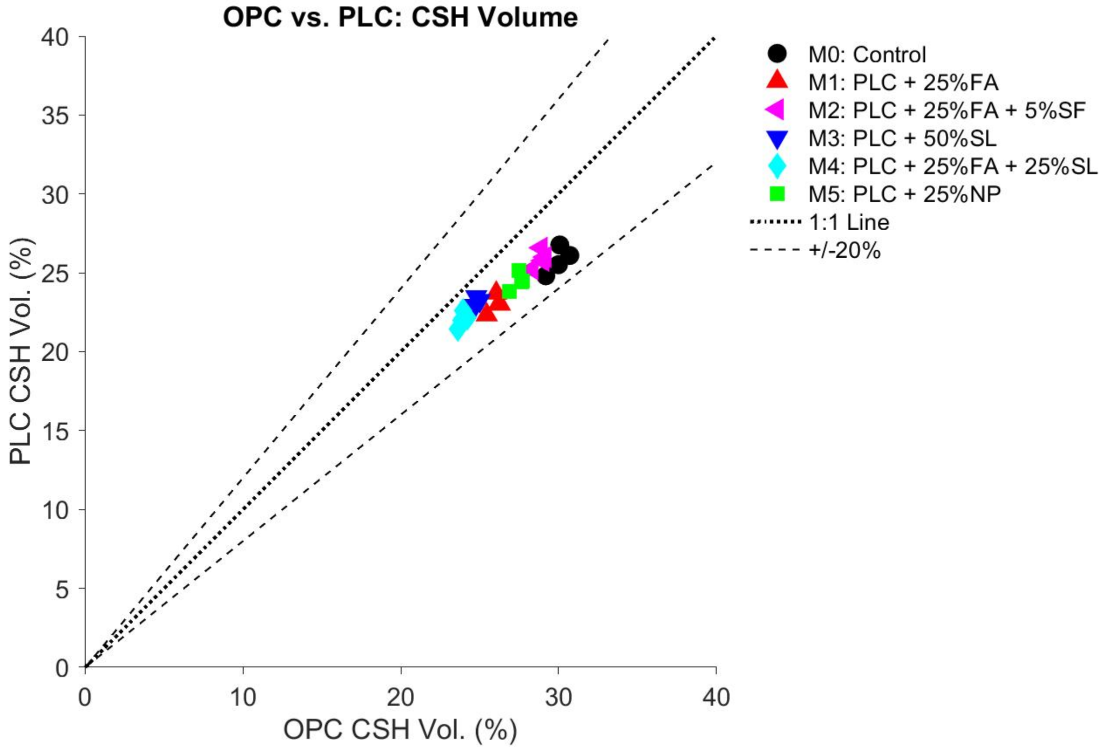
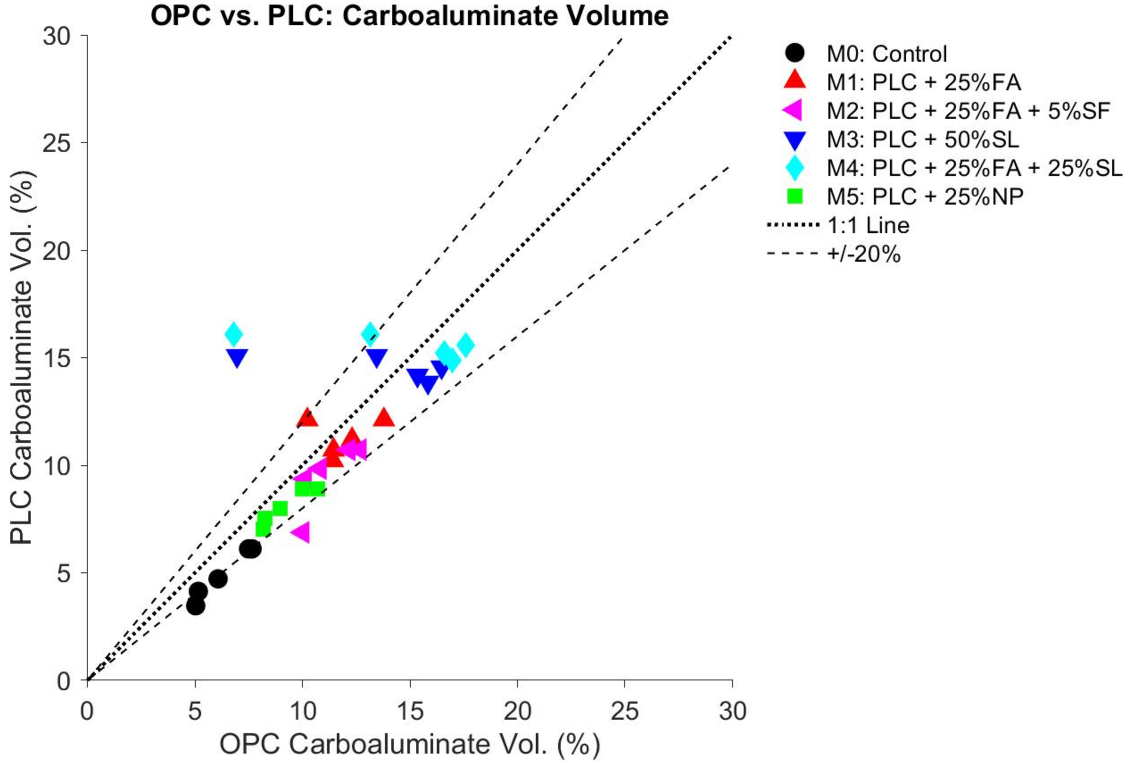
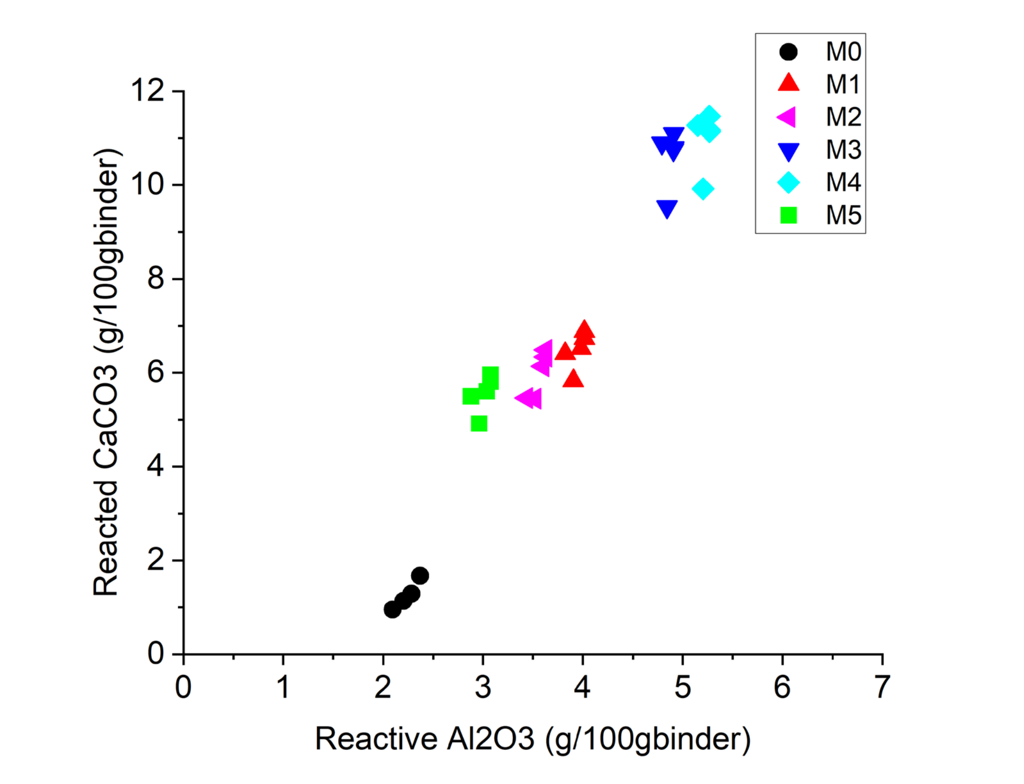




- Slightly lower C-S-H form in PLCs due to dilution of clinker with limestone
- Slightly lower carboaluminates form in PLCs due to dilution

Takeaway #4

- Models generally agree with experimental observations
- Calcite that reacts is linearly proportional to reactive alumina in the system



- PLCs can be used as a direct replacement for OPCs in almost all cases. If SCMs are present, the use of PLCs is recommended over OPCs.

Summary

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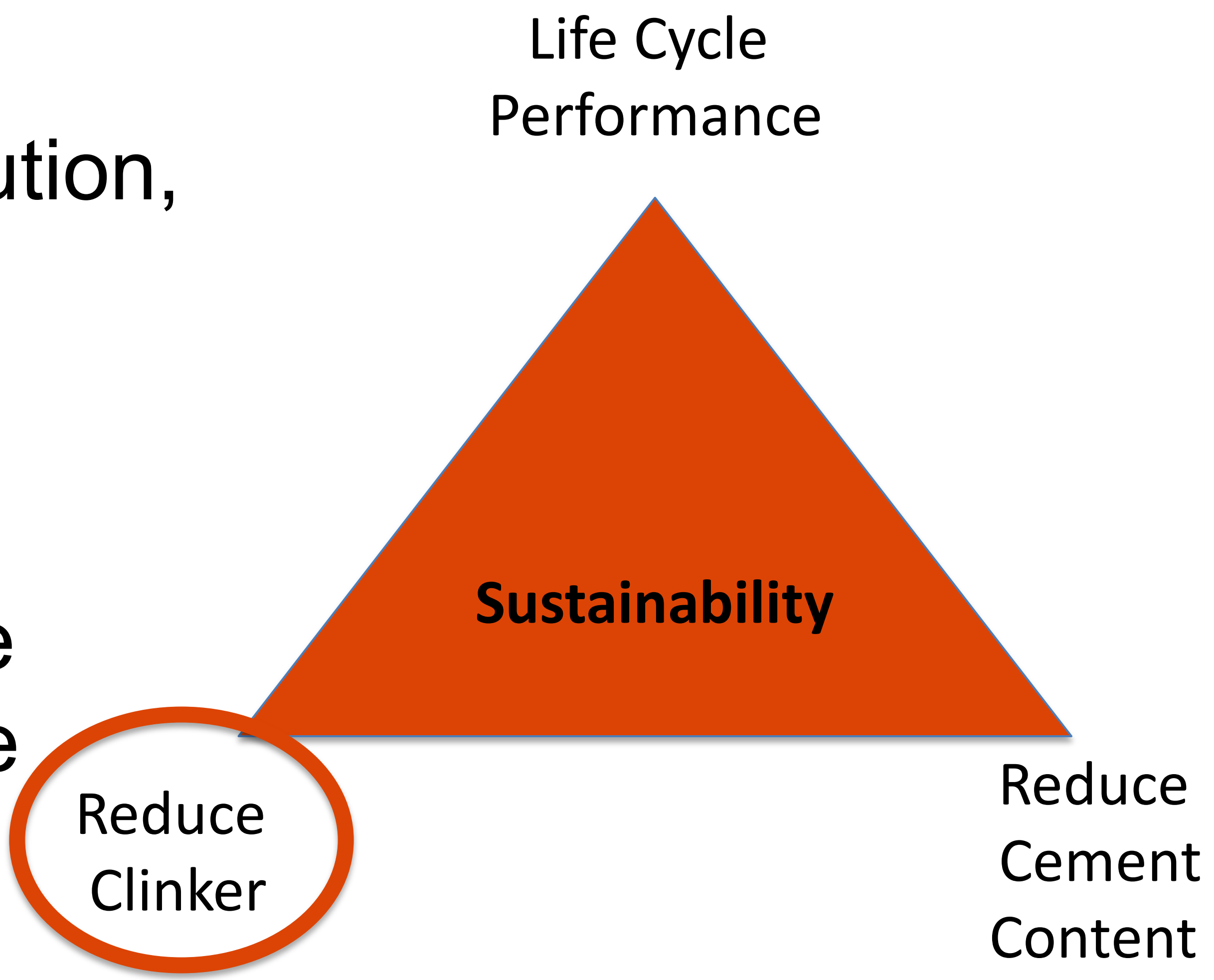
- PLC and Slag reduce CO_2
- Commercially available solution, specifications and codes
- Its all about porosity
- Thermodynamic modeling
- Limestone and Slag are like peanut butter and chocolate
- Alumina in slag (or SCM)



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Challenge

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- Do you want to make your concrete better?
- Do you want to do your part to reduce carbon footprint?
- Do you want to try something with a high probability of success?

- Happy to discuss if C595 and Slags may meet your need