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TRANSPORTATION RESEARCH BOARD

Paving the Way Toward Carbon-Neutral Concrete

November 29, 2021

@NASEMTRB
#TRBwebinar

PDH Certification Information:

1.5 Professional Development Hour (PDH) – see follow-up email for instructions
You must attend the entire webinar to be eligible to receive PDH credits
Questions? Contact TRBWebinars@nas.edu

#TRBwebinar

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REGISTERED CONTINUING EDUCATION PROGRAM

Learning Objective

Discuss how Portland-limestone Type IL cement helps move toward carbon neutrality

Performance of Slag Cement with Portland-limestone Cement in Concrete Reducing the CO₂ Footprint of Concrete

November 29, 2021. TRB Webinar

Doug Hooton

Professor Emeritus,

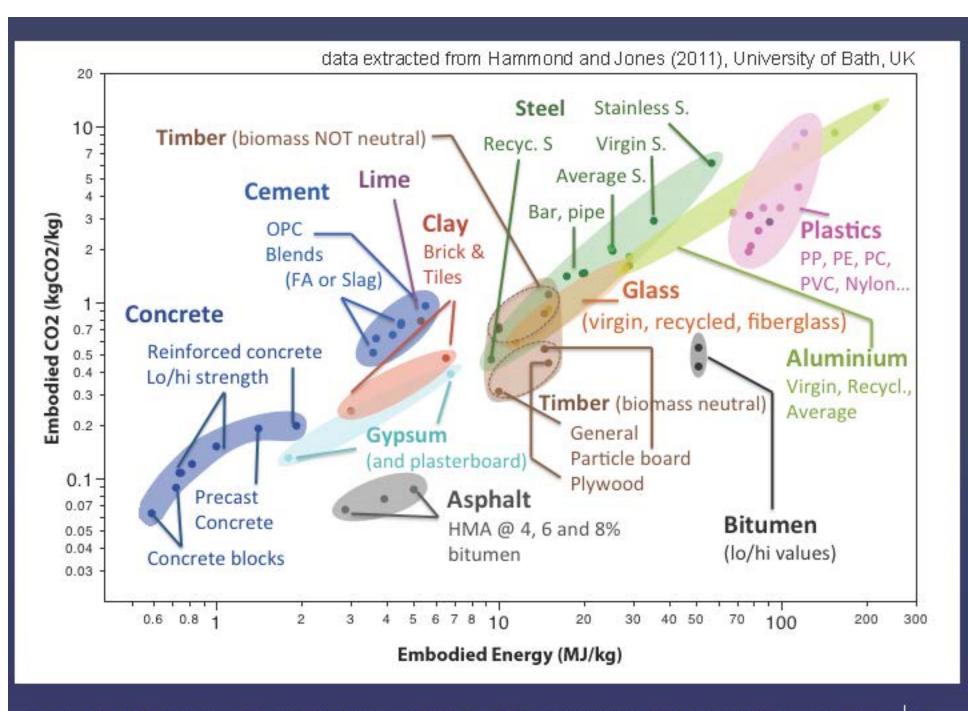


NSERC/CAC Industrial Research Chair in Concrete Durability & Sustainability

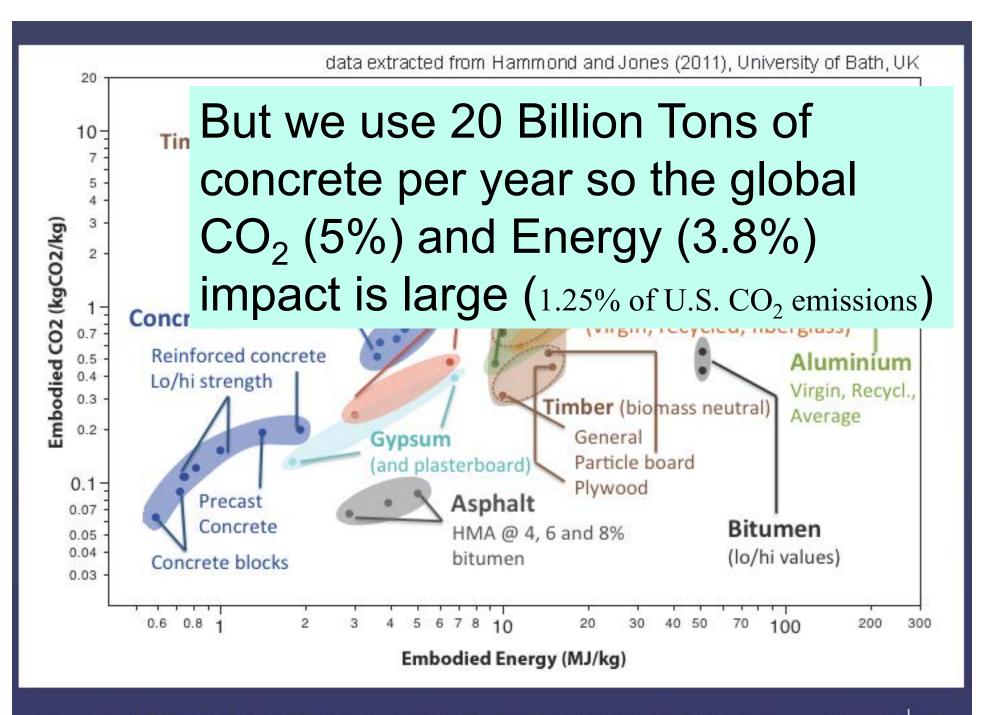
UNIVERSITY OF TORONTO DEPT. CIVIL & MINERAL ENGINEERING

Concrete is a Sustainable Material

- Concrete has the lowest embodied carbon and energy footprint of any construction material (on a kg basis).
- It uses **local materials**, and <u>if properly designed and</u> <u>executed</u>, has a **long service life**, and is **recyclable**.
- If concrete structures are designed for durability, better lifecycle sustainability will be achieved due to longer service life and less repair.



NR MCA INTERNATIONAL CONCRETE SUSTAINABILITY CONFERENCE , SEATTLE – MAY 2012 – BAR CELO, KLINE, WALENTA& GARTNER 8

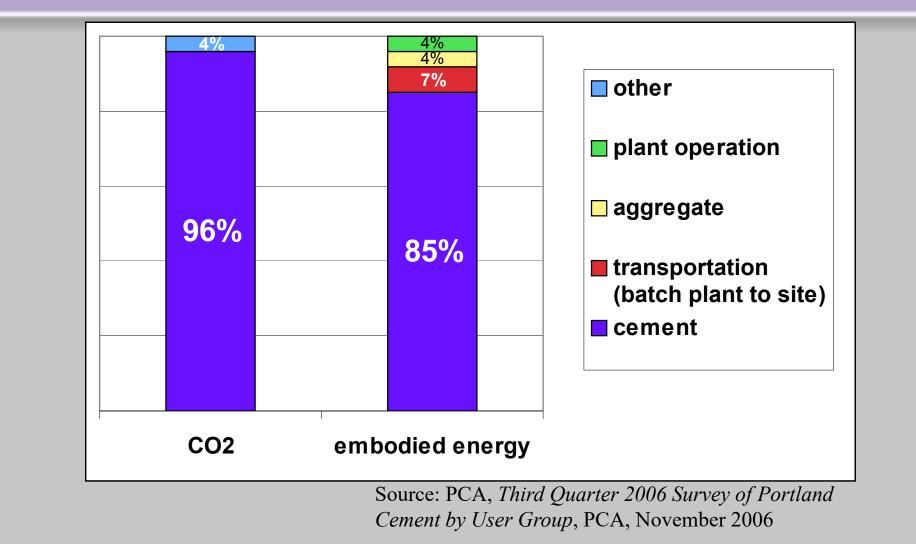


Portland cement is the primary binder in Concrete

- Portland Cement is manufactured from limestone and shale rocks that have been fired at 1450 °C to form a synthetic rock called clinker. This clinker is then crushed to a powder.
- When limestone is heated in the kiln, it gives off CO₂.
 - $CaCO_3 \rightarrow CaO + CO_2$
- This reaction is unavoidable in the manufacture of cement clinker
- So to reduce CO₂ the clinker fraction of cement has to be reduced.



CO₂ emissions and embodied energy in Plain Portland Cement **Concrete**



Future Trends: Emissions Regulations & Portland Cement

- Making Portland Cement produces CO₂
 - From Limestone decomposition (~60%)
 - From fuel consumption (~40%)
- Cement plants reduced energy by 40% & CO₂ by 33% since 1970 (e.g. by more efficient kilns and processes)
- The 2021 PCA Roadmap is to reduce current emissions by 50% by 2030
- Further cuts can only be obtained by reducing clinker content of cements, such as with:
 - Blended cements
 - Type IL Portland-Limestone cements (PLC)
 - Increasing the use of supplementary cementitious materials (SCMs) in concrete



Cutting CO₂ emissions

 Due to increased societal and government pressure, the cement industries in Europe (CEB), North America (PCA) and Globally (GCCA) have developed roadmaps to:

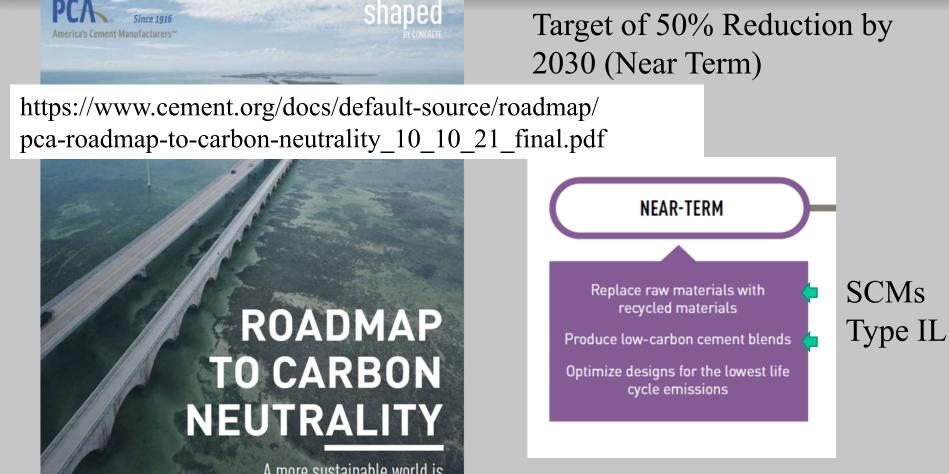
1. reduce CO₂ emissions by 50% by 2030

- This can be attained using currently available options such as PLC and SCMs as well as more waste fuels

2. attain carbon neutrality by 2050

- this will likely require carbon capture and sequestration as well as non-CO2 emitting fuels

Working with the Concrete and Construction Industries, the Cement Industry is Committed to Even Bigger Reductions



A more sustainable world is Shaped by Concrete

Carbon Neutrality by 2050

1+1 = 2 or maybe 3

1 Portland-limestone cements meeting ASTM C595 Type IL, are designed to provide equal performance to Type I cements while providing approximately a 10% reduction in its Carbon footprint.

+ 1 Reductions in carbon footprint of concrete can also be achieved using **SCMs such as slag cement** to lower the cement clinker content.

= 2 These two materials selections can also be used together to further reduce the carbon footprint of concrete.

Or = 3? Interestingly, in some cases early-age performance of slag cement when used with Type IL cement has been found to be equal to or better than with Portland cement from the same source improve constructability.

Why 3?

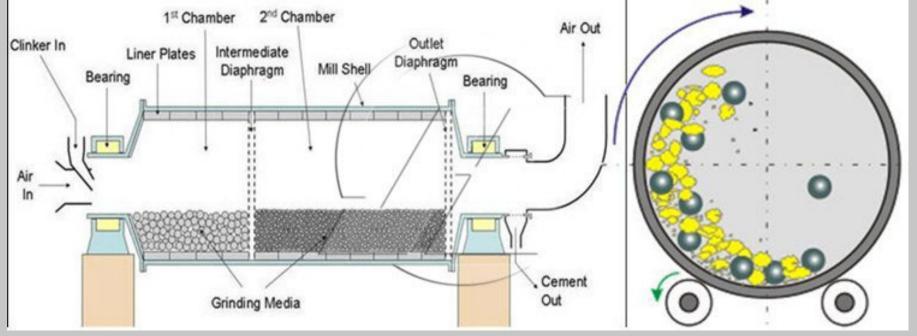
- Using both limestone and slag in combination can lead to significant reductions in the embodied CO₂ associated with concrete while providing excellent concrete.
- The early-age performance of slag cement concrete with Type IL cement has been found to be equal to or better than with Portland cement from the same source.
- The alumina in the slag cement can react with more of the finely divided limestone in Type IL cement to form additional carboaluminate hydrates that then results in reduced porosity and increased early-age strength of concrete.
- There is also reduced permeability, as indicated by ASTM C1202 test results.
- Field trials and use in buildings, pavements and highway structures have shown **equivalent performance** of Type IL-slag binders relative to Type I-slag binders in terms of both mechanical and durability properties.

Portland-limestone Cements (PLC) in North America

- Portland-limestone cements are made from the same components as Portland cements: Clinker, gypsum and limestone---but with about 10% additional limestone.
- Portland-limestone cements have been used under the ASTM C1157 Performance Specification for the last 20 years
- Portland-Limestone cements (CSA Type GUL) were added to CSA A3001 in 2008, with up to 15% interground limestone replacing cement clinker and to ASTM C595 & AASHTO M240 in 2011 (Type IL).
- PLC have to meet the same set times and strength development as portland cement of the same type (eg. GU = GUL; Type I = Type IL)
- In addition, fewer raw materials and less energy are used to produce PLC.
- When properly optimized, the limestone is not inert and contributes to the properties of the cement.

Type I/II: Portland Clinker is ground in ball mills together with ~8% gypsum and ~**3 % raw** *limestone* to make the finished portland cement.



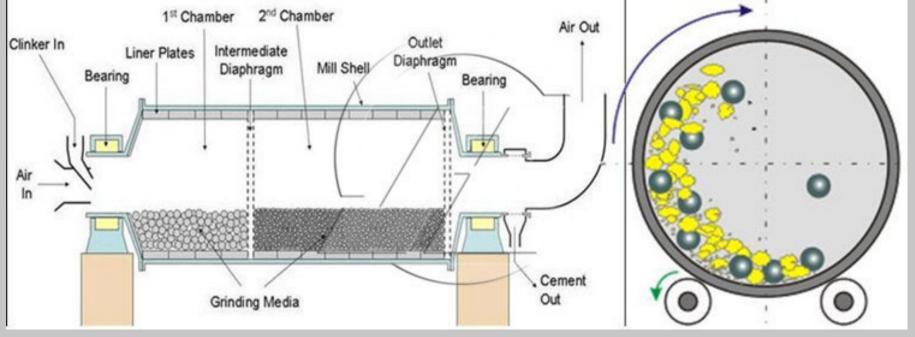


Type IL: Portland Clinker is ground in ball mills together with ~8% gypsum and 10-13% raw limestone to make the finished cement.

(gypsum levels need to be optimized)

Because limestone is softer than clinker, it grinds preferentially, so the cement needs to be ground finer so the clinker component is of equal fineness to get the same strength performance.





Softer limestone gets ground finer than clinker in Type IL

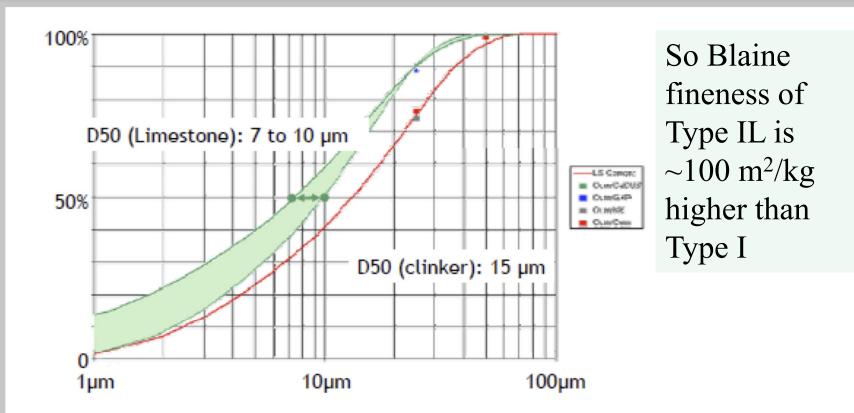


Figure 2.1 Particle size distributions for components of an interground cement. The limestone fraction is finer than ground clinker (Barcelo data as quoted in Hooton 2009).

ASTM C595 / AASHTO M240 / Type IL (CSA Type GUL) Performance

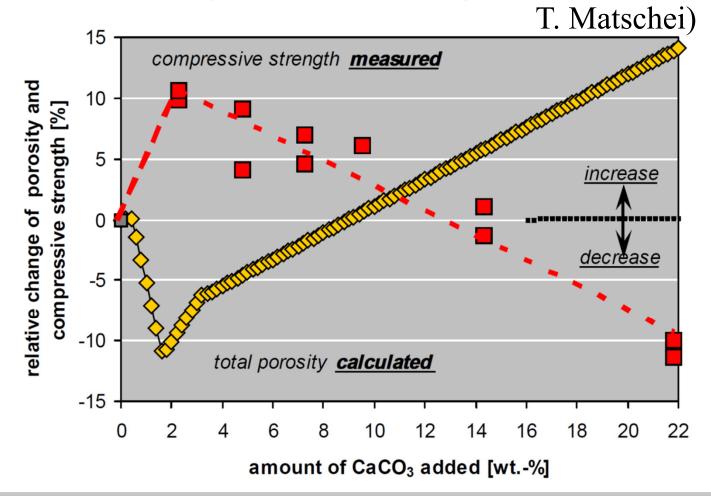
- 1. In ASTM C595, setting times and strength development limits are the same for Type IL as for C150 portland cement of the same type. (i.e equal performance)
- 2. Heat of hydration limits are the same as for Portland cements.
- 3. The only chemical difference is that LOI limits are higher for PLC to account for higher limestone contents.
- 4. In concrete, PLC also performs well with slag or fly ash at normal replacement levels (no need to reduce % SCM)
- 5. In many cases, Type IL+SCM perform better at early age than Type I+SCM, due to nucleation effects of the finer limestone particles on calcium-silicate reactions and due to formation of additional carbo-aluminates.

Background– Portland limestone cements elsewhere

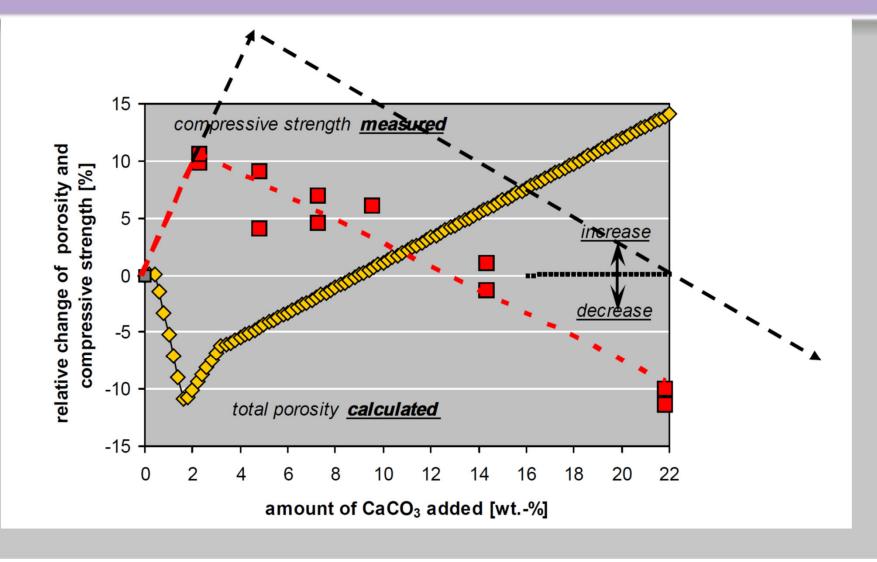
- Used in France since the 1960s
- For over 30 years, the EN197 Cement standard has allowed up to 20% interground limestone in CEM IIA/L cements, and up to 35% in CEM IIB/L cements, in addition to 5% MAC (minor additional components) which also could be limestone.
- Allowed in Canada CSA A3001 as Type GUL since 2008

Better particle packing and increased carboaluminate formation fills in pores and increases strength (Equal strength at ~12-14% limestone)

Correlation: Porosity – Compressive Strength (exp. Data by D. Herfort, Aalborg cement)



When Slag is blended with Type IL, more carboaluminates are formed (more alumina from the slag), so 28-day strengths should increase.



Strengths of Air-entrained Concretes cured at 73 °F with limestone and SCMs

Mix Identification	% clinker		e Streng	ngth (psi)		
(all 400 kg/m3 (666 pcy mixes)	in binder	w/cm	7 day	28 day	56 day	182 day
GU Cement Control	89*	0.40	5700	6600	7350	7630
GU + 40% Slag	53	0.40	4760	6700	7130	7420
GUL15 + 40% Slag	46	0.40	5380	7580	8340	8580
GUL15 + 50% Slag	38	0.40	5260	8020	8710	9510
GUL15+ 6% Silica Fume + 25% Slag	53	0.40	6670	9420	10,160	11,020

* 3.5% limestone and 8% gypsum

U. of Toronto Field site data

ASTM C1202 Permeability Index of Airentrained Concretes cured at 23 °C with GU/GUL cements and SCMs

Mix Identification (all 400 kg/m ³ (666	% clinker	Rapid Chloride Permeabi ASTM C1202 (Coulom			
pcy mixes)	in binder		28 day	56 day	182 day
Type I Cement Control	89	0.40	2384	2042	1192
Type I + 40% Slag	53	0.40	800	766	510
GUL-15% + 40% Slag	46	0.40	749	581	441
GUL-15% + 50% Slag	38	0.40	525	438	347
GUL -5% + 6% Silica Fume + 25% Slag	53	0.40	357	296	300

CSA A23.1 limit is 1500 coulombs @ 91d for chloride exposure

Type IL in Steam Cured Precast (M.Aqel, PhD thesis U. Toronto 2016)

Mixtures: W/CM = 0.34, 450 kg/m³ binder with 5% Silica Fume,

		GU	G	UL		Type	IL = 1	2% lin	nestone
Air (%)		5.2	5	.7					
Slump Flow (m	m)	690	69	95	90 80	6.6 hours @ 82°C [180°F]			\backslash
Age	Compressive Strength (N				70 60 O	16°Chaur (s) ??	8.1 hours	s @ 70°C [158°F]	16°Chour [61°F[hour]
	55 °C (131 °F) 70 °C			158 °F)	°) 50	Ch Ch			1ºEIP
	Type I	Type IL	Type I	Type IL	05 (°C) 07 05 00 07 00 00000000				lour
16h	47.8	55.3	59.7	60.4	E 30				\setminus
3d	58.9	60.1	62.6	62.5	20	<		95% RH	\longrightarrow
7d	64.5	65.7	66.0	66.2	10	0 2	4 6 8	10 12	14 16
28d	72.5	71.1	70.1	70.4			Steam Cur	ring Duration (hour)
300d	89.3	84.9	82.9	81.1					
28 day RCPT (Coulombs)				Freeze	/Thaw Dur	ability Fac	ctor (%)		
55 °C	55 °C 70 °C			55 °C 70 °C		°C			
Туре І	Type IL	Type I	Ту	vpe IL		Type I	Type IL	Type I	Type IL
616	715	1050	1	.106		98.0	97.1	68.4	83.1

estone

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Drying Shrinkage CSA A23.1 (ASTM C157) w/cm = 0.40 mixtures

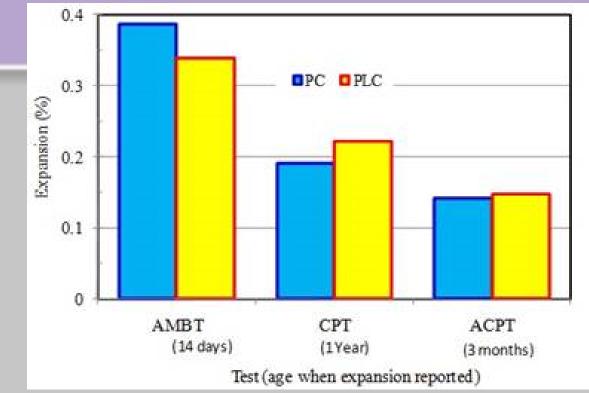
Length Change (%)	GU 100%	PLC10 100%	PLC15 100%	GU 70% SLAG 30%	PLC10 70% SLAG 30%	PLC15 70% SLAG 30%
28 days	0.036	0.037	0.037	0.026	0.027	0.025
1 year	0.069	0.061	0.062	0.058	0.052	0.053
2 years	0.067	0.068	0.065	0.062	0.06	0.067

•Shrinkage was unaffected by PLC (Type IL)

•Reduced 28-day shrinkage with slag mixes

Alkali-Silica Reaction

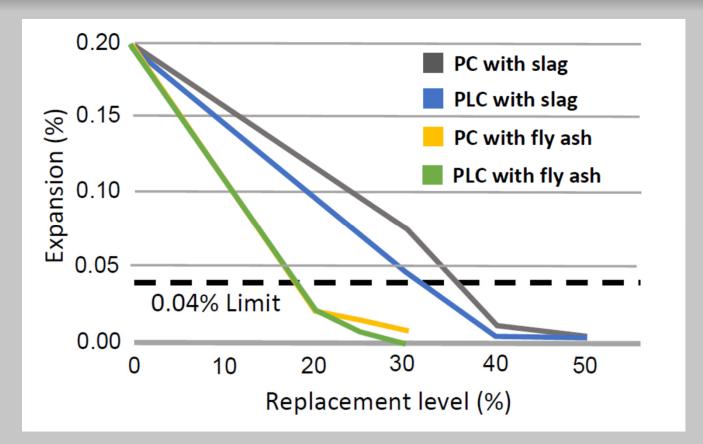
PCA SN3148 Weiss, Thomas & Tennis



Also no difference in the level of SCMs needed to mitigate ASR expansion. (M. Thomas)

Expansion of mortar bars and concrete prisms containing an alkali-silica reactive aggregate (siliceous limestone from the Spratt quarry in Ontario). (ACPT is similar to the CPT except specimens are stored at 60°C). The data show that there is **no consistent difference** between expansions produced with PC compared with PLC.

ASR: 2-year ASTM C1293 Expansions



Thomas et al 2013

Freeze-Thaw and Scaling Resistance

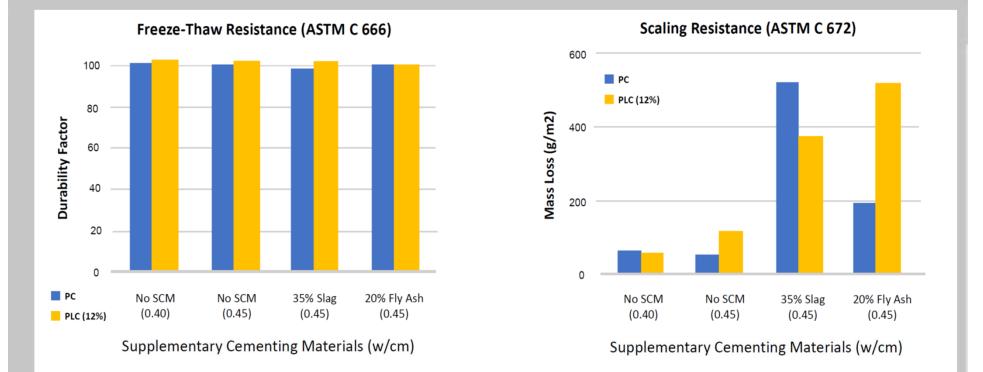
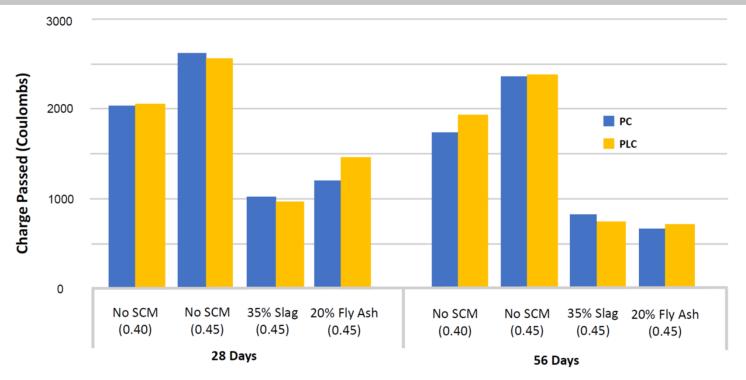


Figure 3: Results of freeze-thaw and de-icer salt scaling tests for PC and PLC concretes with and without SCM (Thomas and Hooton 2010)

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Index of Chloride Penetration Resistance ASTM C1202 Coulombs

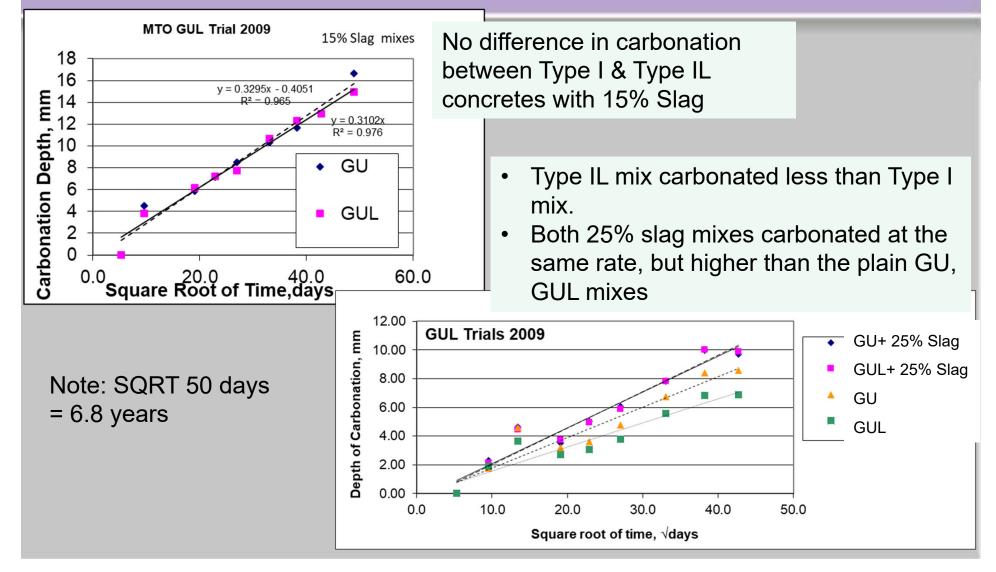


Supplementary Cementing Materials (w/cm)

Figure 4: "Rapid Chloride Permeability Test" (ASTM C1202) data for PC and PLC concrete with and without SCM (Thomas and Hooton 2010)

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Two Carbonation Studies (U of Toronto) 7-day moist cured concrete prisms (w/cm = 0.40) stored at 50% rh and 23 °C



Sulfate Resistance

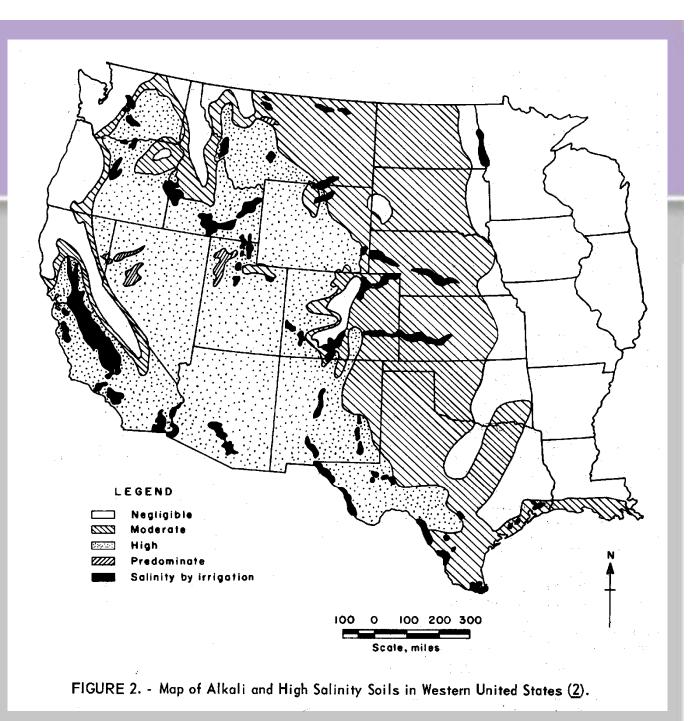
While some early published papers indicated a potential concern for an increased risk of low-temperature thaumasite sulfate attack, extensive long-term tests on concretes have shown that Type IL cement- slag cement combinations are as resistant to sulfate attack as Type I cement-slag cement combinations and more resistant than equivalent w/cm concretes made with Type V cements to both the ettringite and thaumasite forms of degradation.

Sulfate Soils in Western USA

Reportedly, sulfate concentrations can exceed 20,000 ppm.

And the west is mostly arid, which concentrates salts

Ref: USBR soils map, where alkalinity = alkali sulfates



Sulfate Resistance: 2016 PCA Report based on 10 years of lab and field testing

1916–2016 Celebrating 100 Years of Excellence



Research & Development Information

PCA R&D SN3285b

http://www.cement.org/pdf_files/sn3285b.pdf

Sulfate Resistance of Mortar and Concrete Produced with Portland-Limestone Cement and Supplementary Cementing Materials: Recommendation for CSA A3000

More recent 2018 and 2021 findings have not changed

by R. D. Hooton and M. D. A. Thomas

Thaumasite Sulfate Attack (TSA)



- A relatively unusual form of sulfate attack usually associated with low temperatures (0-10°C) and very wet environments.
- Triggered by soluble carbonates and sulfates, and associated with low temperatures .
- The C-S-H and Ca(OH)₂ are converted to gypsum and thaumasite.

 $Ca_{6}[Si(OH)_{6}] \cdot (SO_{4})_{2} \cdot (CO_{3})_{2} \cdot 24H_{2}O$

or: $CaSiO_3 CaCO_3 CaSO_4 15H_2O$

U of T Concrete Sulfate Resistance Program PhD of Reza Ahani, 2019

- 53 concrete mixtures (cast 2010, 2011, 2012): Still being monitored
 - W/CM = 0.4, 0.5, and 0.7,
 - Cements: GU, PLC (9, 10.5, and 15), 3 HS, 2 HSL, 2 MS, and HSb,
 - SCMs: 40 & 50% slag, 8% silica fume, 15% metakaolin, and 25% fly ash.
- Evaluation of sulfate resistance:
 - Measurement of length and mass changes (Lab: every 1.5m / Field: annually),
 - Making visual inspections (Lab: every 1.5m / Field: annually),
 - Mineralogical analysis (X-Ray diffraction) on damaged concrete prisms,
 - Microstructural analysis (Micro X-ray fluorescence spectrometer and scanning electron microscope) on damaged concrete prisms.
- Other tests:
 - Compressive strength (7d, 28d, 56d, 6m, and 1y),
 - Rapid chloride permeability (28d, 56d, 6m, 1y, 2y, and 3y),
 - Bulk resistivity (6m, 1y, 2y, and 3y).

UofT Field sulfate exposure started in 2010

- A trench dug to 2.5m deep,
- Located in Toronto,
- Variable underground temperatures of 3-16 ° C,
- Field prisms: 75×75×285 mm,
- For each concrete mixture:
 - 3 prisms in limewater,
 - 3 prisms in Na₂SO_{4,}
 - 3 prisms in MgSO₄.
- SO₄-² concentration:
 - 0.40 mixtures: 15,000 ppm,
 - 0.50 & 0.70 mixtures: 1,500 ppm.

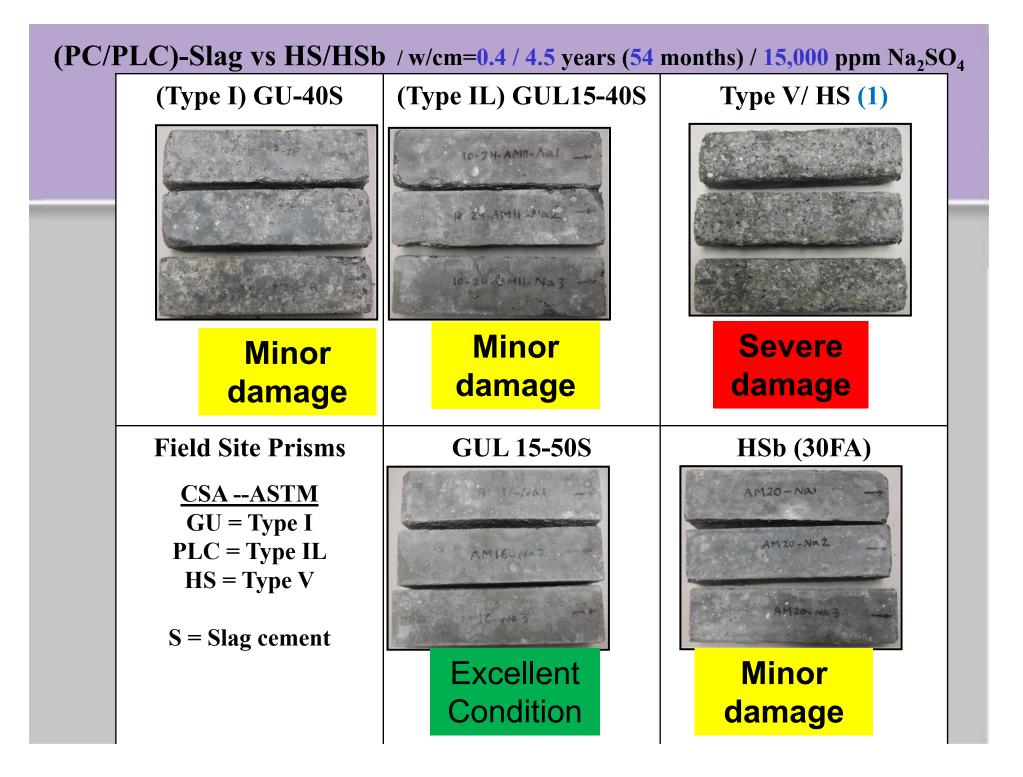


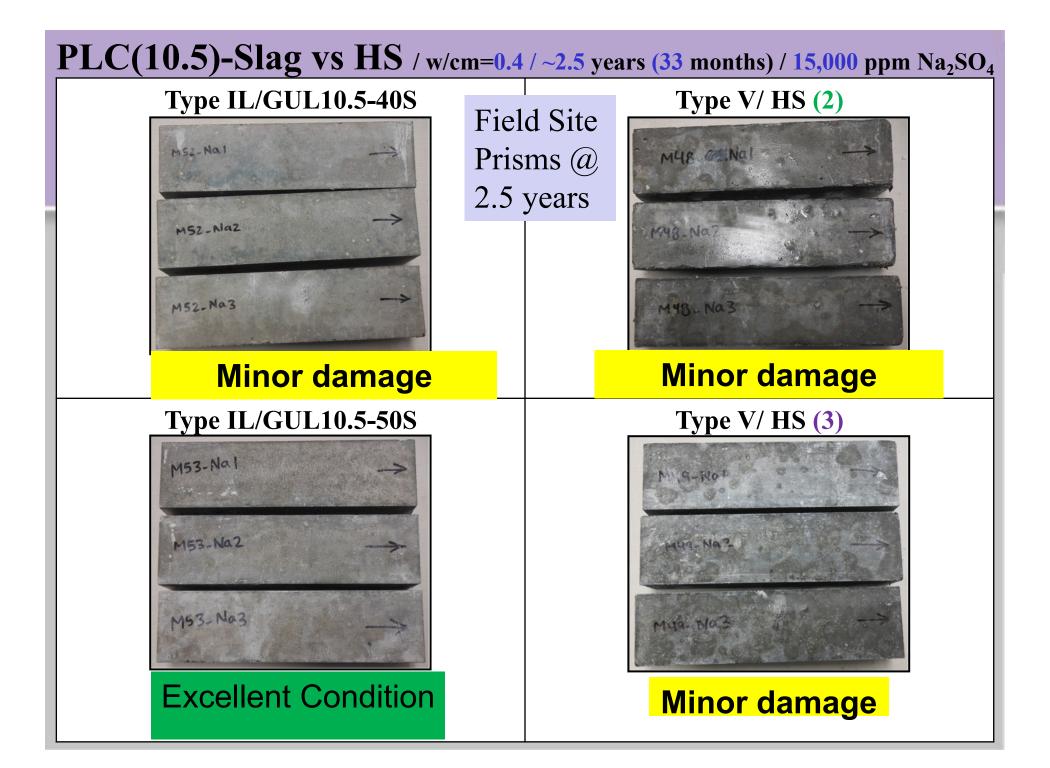






UofT Visual Condition Rating od Concrete	Label [Num. Rating]	Example Photos
Excellent Condition – No visible damage	UND [0]	МЗя-сн2 ->
Minor damage <u>Slight</u> mass loss and/or cracking at some corners and/or some longitudinal edges	MIN [1]	AM20-Nai ->
Minor to Moderate damage <u>Slight to moderate</u> mass loss and cracking at some corners and/or longitudinal edges	MIN- MOD [2]	~10.24-AM8-7G
Moderate damage <u>Moderate</u> mass loss and/or cracking at some corners and/or some faces Localized scaling at some faces	MOD [3]	AM 32-Na ²
Moderate to Severe damage <u>Moderate to severe</u> mass loss and/or cracking at most of the faces and corners Widespread scaling at most of the faces	MOD- SEV [4]	
Severe damage <u>Severe</u> mass loss from all faces and ends. Complete peeling of surface paste from all faces and both ends	SEV [5]	





(PC-Slag / PLC-Slag) vs (HS / MS) --- Field Exposure After ~5.5 years exposure to Na₂SO₄ (3-16 °C) Effect of W/CM

W/CM = 0.40 (in 15,000 ppm) vs W/CM = 0.50 (in 1,500 ppm)



Conclusions from UofT and UNB (M. Thomas) Concrete Sulfate Resistance Tests

- 1. The addition of supplementary cementitious materials to the concrete greatly improves resistance to external sulfate attack.
- 2. Many SCM-blend concretes with GU and GUL cements are out-performing Type HS concretes
- 3. No consistent trend noted as a function of limestone content; concretes with GU or GUL and the same SCM contents show similar performance.
- 4. CSA A3004-C8 Procedure B (5 °C ASTM C1012 mortar bar test adopted in 2010—**and deleted in 2018**) does not reliably predict concrete performance and should not be used to evaluate acceptability of cementing materials.

ASTM, AASHTO, and ACISpecifications allow Type IL for Sulfate Resistance

- PLC (up to 15% limestone) was included in ASTM C595 & AASHTO M 240 in 2012 as Type IL.
- Based on results of this sulfate research, in 2016 ASTM & AASHTO permitted Type IL+SCM combinations in all sulfate exposures. The only requirement is that ASTM C1012 expansion limits be passed----using the same limits as for blended cements without limestone.
- ACI 318-19 removed previous restrictions on use of Type IL in sulfate exposures.

Examples of Concrete Performance with GUL (IL) + Slag

Concrete Performance Data from: MTO Highway projects in Ontario

Note: in Canada, Slag is only widely available in Ontario

Trial 1: Ontario Highway Field Barrier Wall Nov. 4, 2009

- Dufferin Construction Barrier Wall Test sections 23m³ of PLC+15% Slag vs GU+15% Slag (CM = 355 kg/m³)
- On Queen Elizabeth Expressway in Burlington
- First MTO trial of PLC
- Testing performed by Dufferin and University of Toronto, with scaling slabs also tested by MTO.

PLC Barrier Walls on QEW Nov. 4, 2009



23 m³ of each mix placed, 30 MPa, 60-100 mm (2.5-4 in.) slump

Nov. 2009 Barrier Wall

2009 Barrier Wall	PC +15% SLAG	PLC + 15% SLAG
Shrinkage (28d)	0.038%	0.038%
Strength (MPa)		
1	9.5	10.3
3	19.3	19.4
7	25.6	26.8
28	36.9	37.9
56	38.9	38.0
91	40.7	40.2
Freeze/Thaw Durability	94%	94%
MTO LS-412 Scaling	0.24 kg/m²	0.24 kg/m²
RCP (Coulombs)		
28 days	2070	1490
56 days	1930	1340

Trial 2: PLC Paving on Highway 401 Off Ramps at Hwy 10, Sept 27, 2010

Cooperation between MTO, Dufferin Construction, Holcim and University of Toronto





PLC Paving Trial

- Highway 401 East bound exit to HWY #10 from collector lanes.
- 100 m of paving was done with PLC+25% Slag as binder, otherwise identical to GU+25% Slag control mixture. 1.5 in. (37 mm) Aggregate
- Pavement was 14 ft (4.25 m) wide x 11 in. (280 mm) thick with pre-placed dowel baskets
- ~8m was wet-cured and rest used normal curing compound



Portable Central Mix Plant

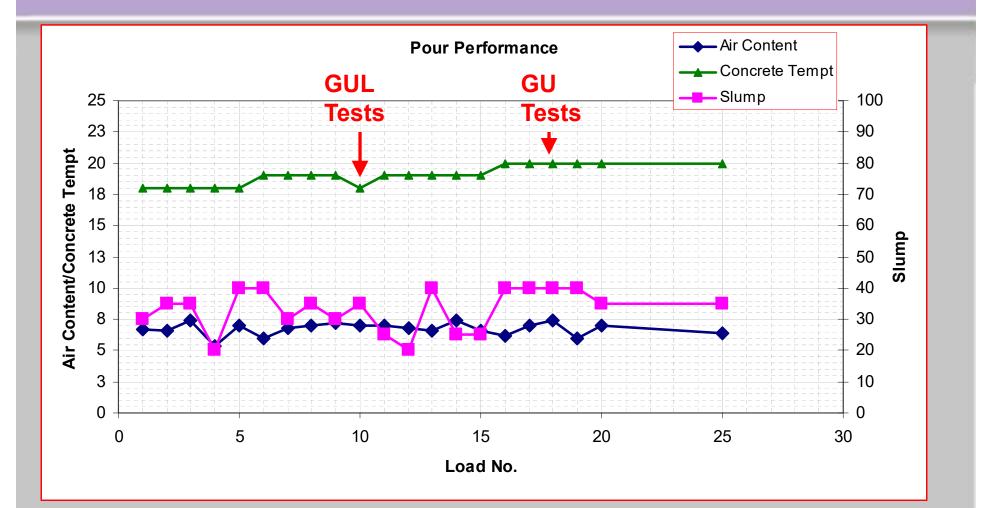
Preplaced dowel baskets



GUL on Left and GU on Right (after tyning but before curing compound)



Test Data by Truck Load



Hardened Test specimens taken from Indicated Loads

Tested Loads	GU Control + 25% Slag	GUL + 25% Slag
Slump (mm)	35	20
Air (%)	5.4	4.6
Temp.	18	19
w/cm	0.42	0.435
Strength (MPa)		
7 day	35.0	31.9
28 day	50.4	48.9
56 day	52.3	49.3
91 day	55.8	55.6
Split Tensile (MPa)		
7 day	3.3	3.0
28 day	4.3	4.0
Flexural (MPa)		
7 day	5.8	5.2
28 day	7.4	6.8

Pavement Data (for the 2 trucks sampled)

	GU Control + 25% Slag	GUL + 25% Slag
Air (%)	5.4	4.6
Hardened Air (%)	5.3	3.4
Spacing Factor (um)	0.135 [0.0053 in.]	0.123 [0.0048 in.]
RCP (coulombs)		
(100x200 mm cyl.) 28d	835	985
56d	702	770
99d	660	677
(cored 150x300mm cyl.) 28d 56d	1215 812	1254 794
Cores from Pavement 28d	2009	2261
99d	972	983
28d drying shrinkage (%)	0.023	0.022

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99d	972	983
28d drying shrinkage (%)	0.023	0.022

Paving mixes: Freeze/Thaw and Scaling on test slabs (and no scaling observed in the pavements after 10 years)

	GU Control + 25% Slag w/cm = 0.42	GUL + 25% Slag w/cm = 0.435
ASTM C666 F/T	Hardened air =5.3%	Hardened air = 3.4%
Durability Factor (%)	94.3	91.8
Mass Loss (%)	0.096	0.114
LS-412 Scaling Mass Loss (kg/m ²)	0.88	1.37

Paving Mixes: Chloride Bulk Diffusion ASTM C1556 (10⁻¹² m²/s)

	GU Control + 25% Slag	GUL + 25% Slag
28 days	4.8	6.2
91 days	5.4	3.4

Trial 3: Slip Formed Barrier Wall (Highway 402 near Sarnia Ont.)

- Cement/Concrete supplied by St. Marys Cement/CBM, with private paving contractor working on MTO project.
- A test section and a control section of barrier wall were slip formed on Nov. 3, 2011.
- Both sections had 25% slag and the portland-limestone cement (GUL) had ~11% limestone
- The highway was opened shortly afterwards and was exposed to salt splash.



Highway 402 Sarnia Barrier Wall Data

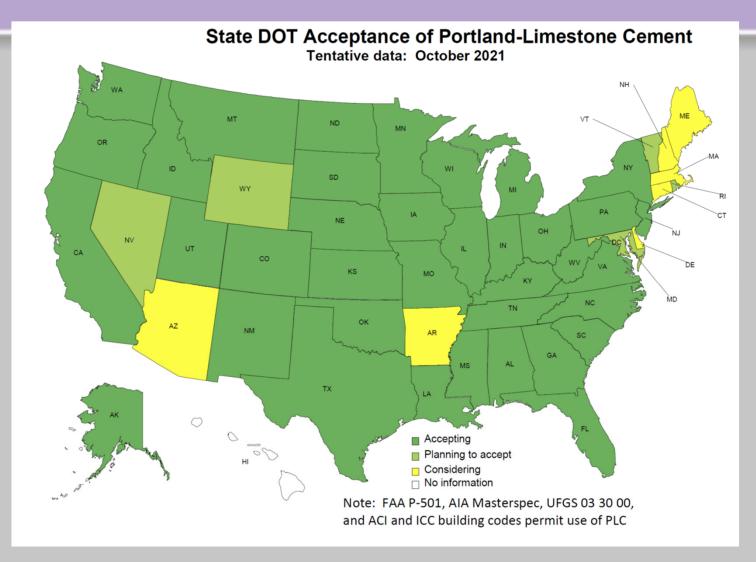
	GU + 25% Slag	GUL + 25% Slag
ASTM C1202 56d cores (coulombs)	1212	894
Bulk Resistivity 56d cores (Kohm-cm)	141	189
ASTM C666-A Durability Factor (%)	93.9 (300 cycles)	90.2 (300 cycles)
Scaling Mass Loss ASTM C672 (kg/m ²)	0.32 (50 cycles)	0.27 (50 cycles)

PLC use is not new: over 100 miles of paving with PLC in Colorado and Utah with PLC supplied by Holcim (2007-2011)-often together with fly ash

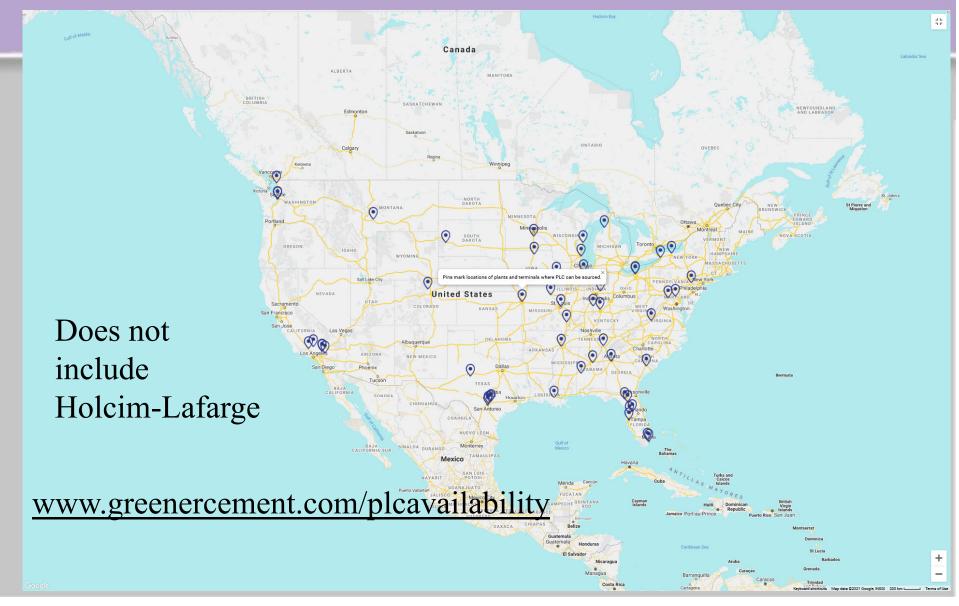


Performance & Lower Environmental Impact

Status of PLC Acceptance by 38 DOTs (Oct. 2021)



Availability of PLC from PCA Member company terminals Oct. 2021 (increasing on a month by month basis)



Type IL Summary

- Portland-Limestone cements are allowed in ASTM & ASSHTO Specifications and in ACI 318 as well as by most DOTs.
- They have been used successfully in many different applications including buildings, pavements, and both cast and slip-formed barrier walls. And in some areas, Type IL is becoming the main cement being used (in 2022, Ontario will likely be 100% GUL).
- Use of Type IL should not affect concrete properties or construction practices when switching from Type I/II.
- Type IL works well with slag (and other SCMs) at normal cement replacement levels. –so both can be used simultaneously
- Type IL provides a 10% reduction in CO₂ emissions from cement plants and reduces the carbon footprint of concrete by an additional 10% without affecting performance or durability
- Type IL with 25% slag can reduce CO₂ emissions by ~35% over an equivalent Type I/II mixture.

Using Portland-Limestone Cement together with Slag Cement makes "Greener" Concrete





COLLEGE OF ENGINEERING School of Civil and Construction Engineering



Keshav Bharadwaj, Antara Choudary Graduate Student Burkan Isgor, Professor, Oregon State University Jason Weiss, Edwards Distinguished Professor, Oregon State University

November 29th 2021

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Cement (Concrete) Industry Is at Center of Climate Change Debate

The New York Times

https://www.nytimes.com/2007/10/26/business/worldbusiness/26cement.html

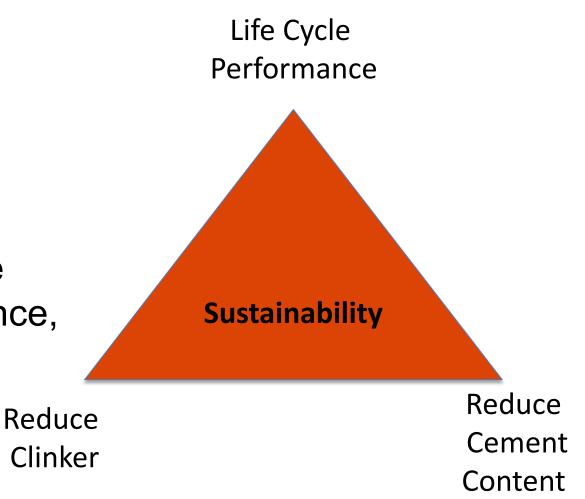
What Can We Do?

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

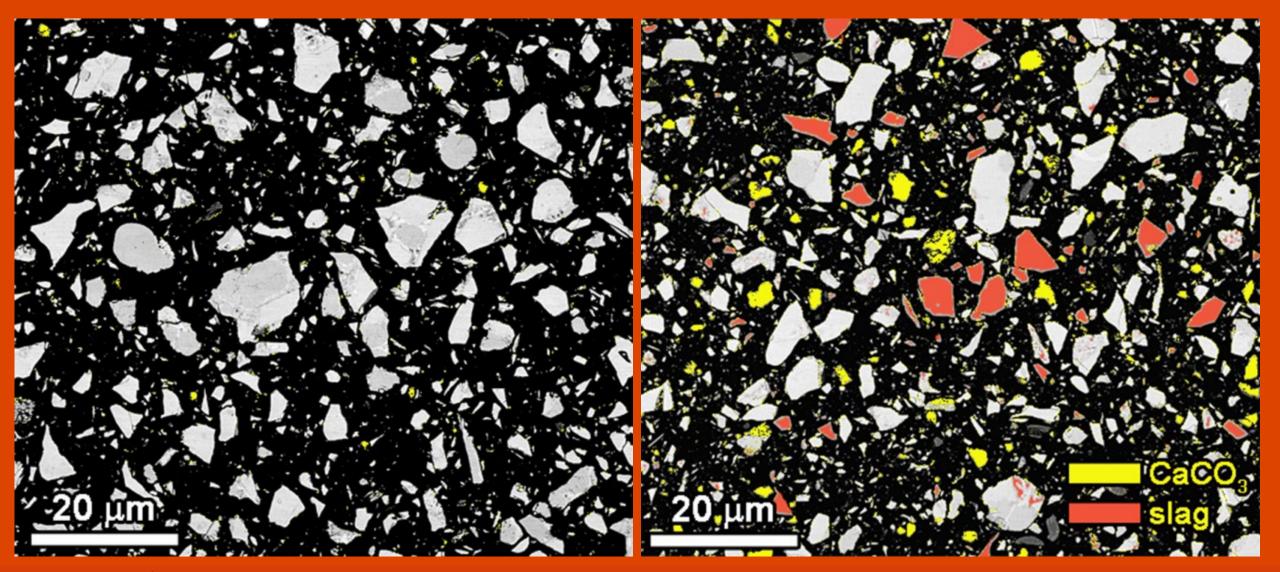


Concrete Sustainability

- Change is needed
- Three prong approach
- Today let's talk
 - PLC to reduce clinker,
 - Improve SCM testing to reduce cement and improve performance,
 - Utilize new mixture design approaches based on performance



Which Cement and Why



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Which Cement and Why

Similar or Improved Performance with

PLC 11% less CO₂/Clinker

PLC-Slag 40% less Clinker

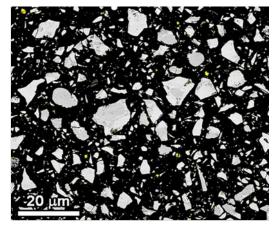


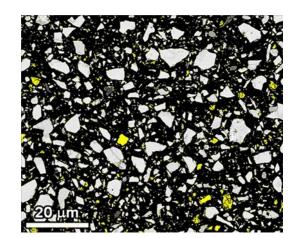
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Portland Limestone Cement Similarities and Differences

OPC - ASTM C150



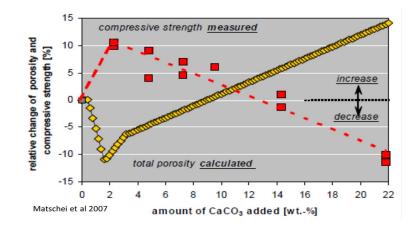


PLC - ASTM C595 IL

- Generally, there is about 10% more limestone in C595 than C150
- C595 cements are an 'engineered system'
 - Not simply diluting the cement
- C595 cements are finer
 - Accelerated rate of reaction (overcomes dilution)
 - Limestone is softer than clinker therefore finer
- C595 cements can have some advantages space filling, nucleation, chemical reactions

Altering Porosity Magic or Science





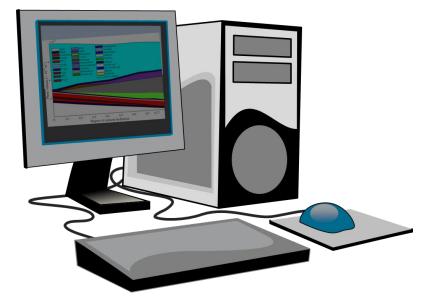
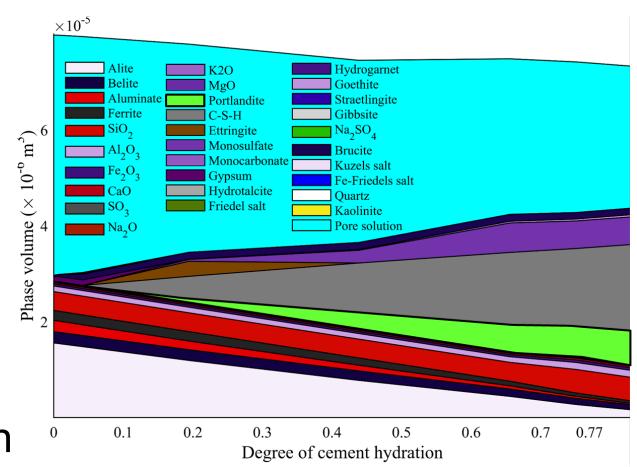


Photo 135078051 © Bblood | Dreamstime.com

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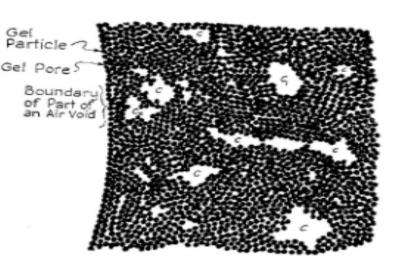
Thermodynamic Model

- Using GEMS to predict the reacted products
- Developed tools for changing SCMs
- Set of well established rules
- Goal is to allow us to determine the reaction
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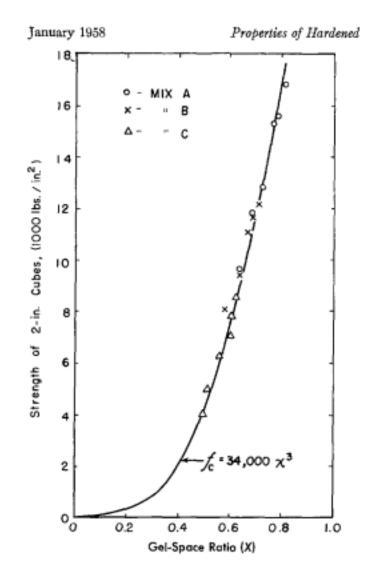


Pore Structure

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



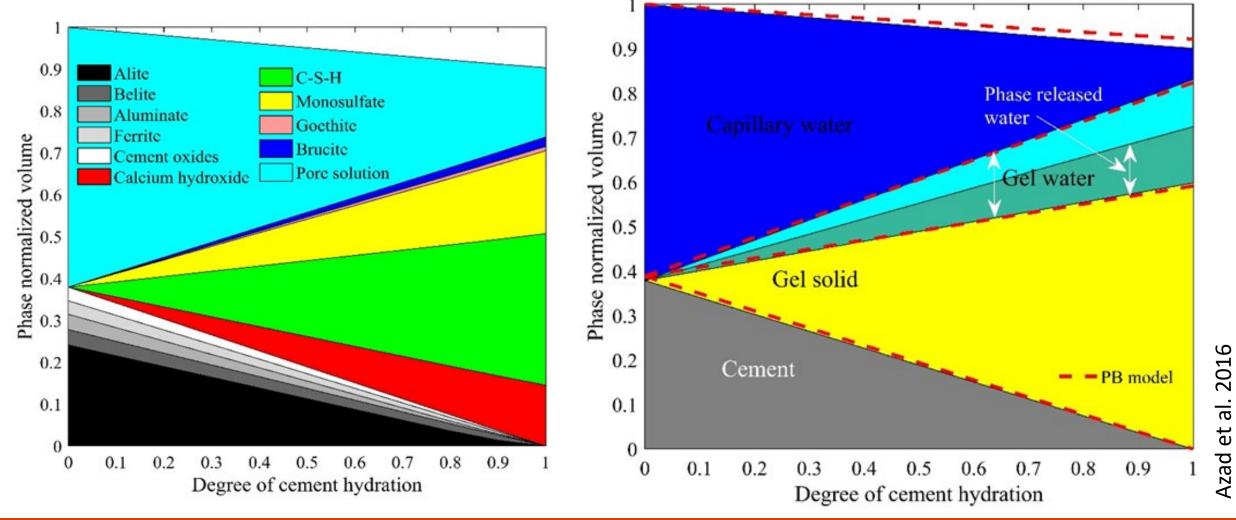
- Gel pores are the pores in the C-S-H gel (2-5 nm)
- Capillary pores (5 nm-10 μm) are the remnants of the space between the cement particles



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Pore Partitioning Powers to GEMS



Comparing Reactions

- In the PLC (as compared to OPC):
 - Similar volume of C-S-H
 - Ettringite and hemi/monocarbonate form instead of monosulfate

45%

35%

30% -

OPC

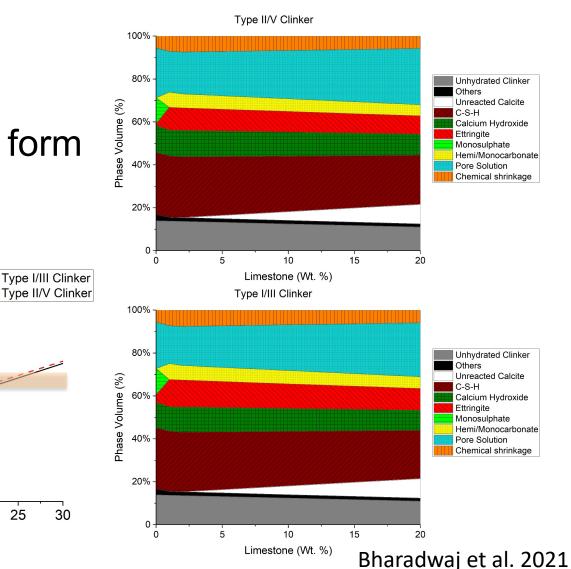
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10

- Calcium hydroxide is 1-2g lower
- Porosity decreases with the addition of A0% ' 0% to 2% limestone
- Additional limestone increases porosity

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Goal is similar porosity



15

Limestone (Wt. %)

20

25

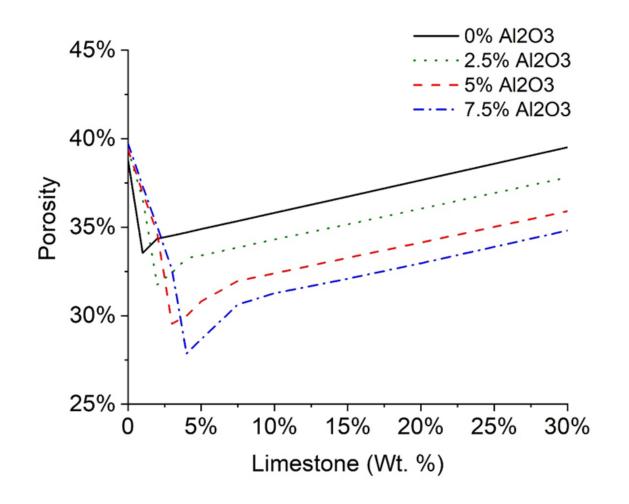
requently sked uestion do I need to stop

Photo 72394692 / Faq © Weerapat Wattanapichayakul | Dreamstime.com

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Can SCM be Used ?



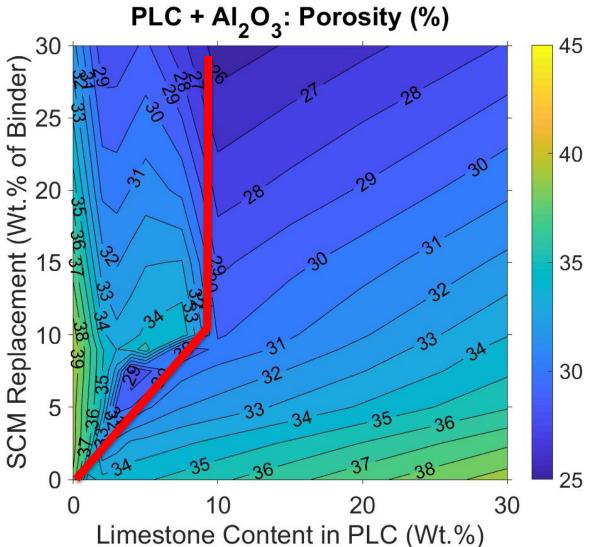
- We have been asked many times if the use of PLC means that we can't use fly ash or slag
- PLC use should not limit SCM usage
- In fact, you can see that there is an additional synergy
- Limestone reacts with Al₂O₃ to form Hemicarbonate and Monocarbonate

Bharadwaj et al. 2021

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When SCM is Used

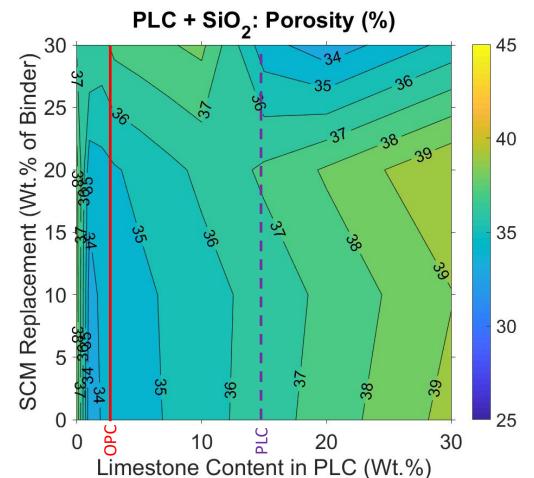
- A plot of porosity when a completely aluminous addition is provided
- Movement from ~ 38 to 39% porosity occurs
- Low porosities can be obtained when SCM is used
- This translates into improved a performance



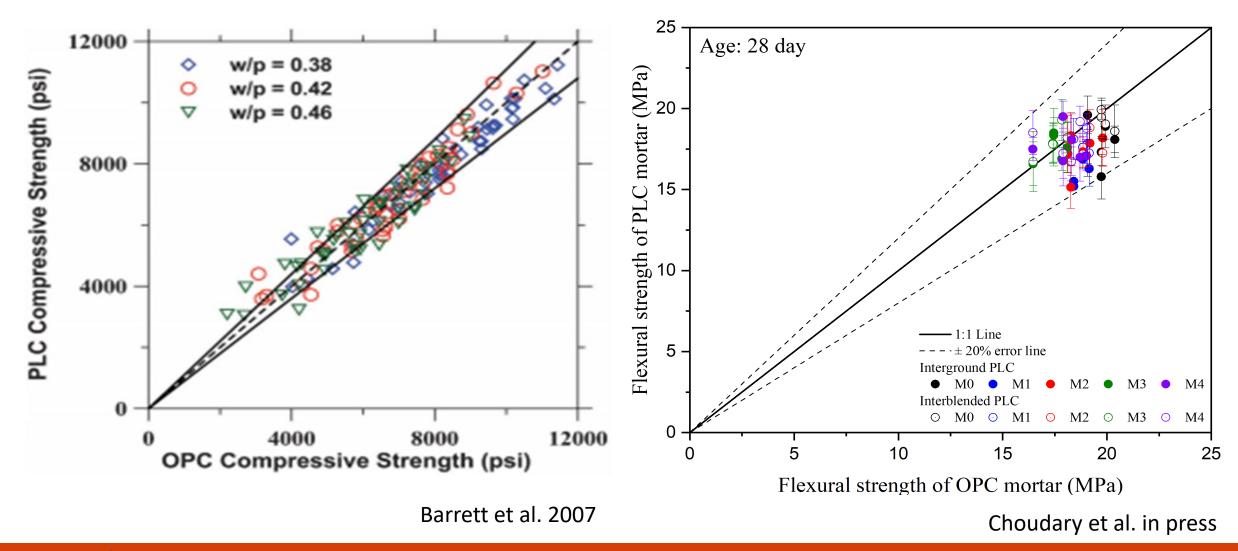
Bharadwaj et al. 2021

PLC + SCM (SiO₂)

- 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

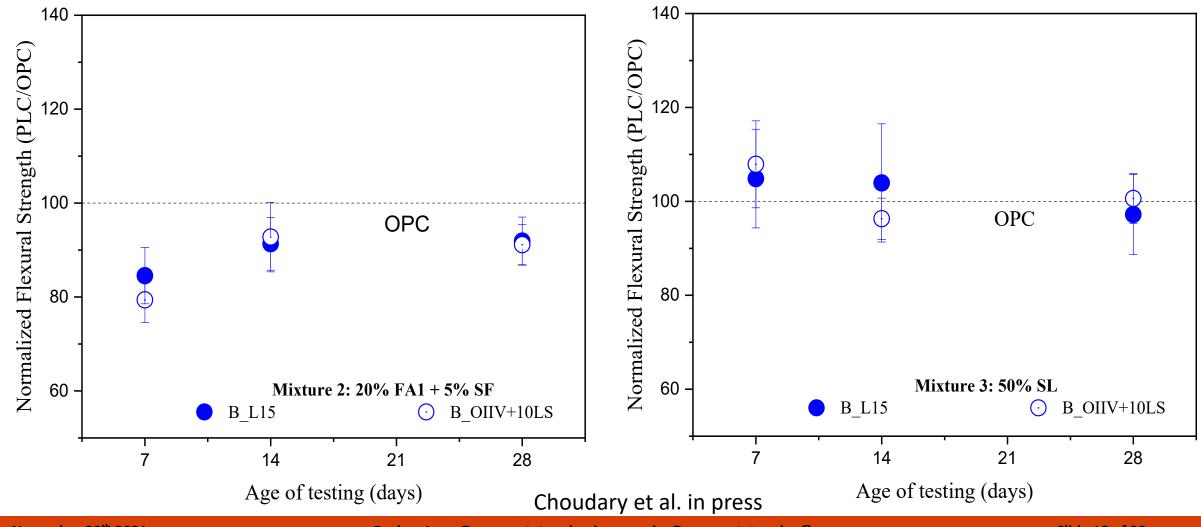


Measured Strength



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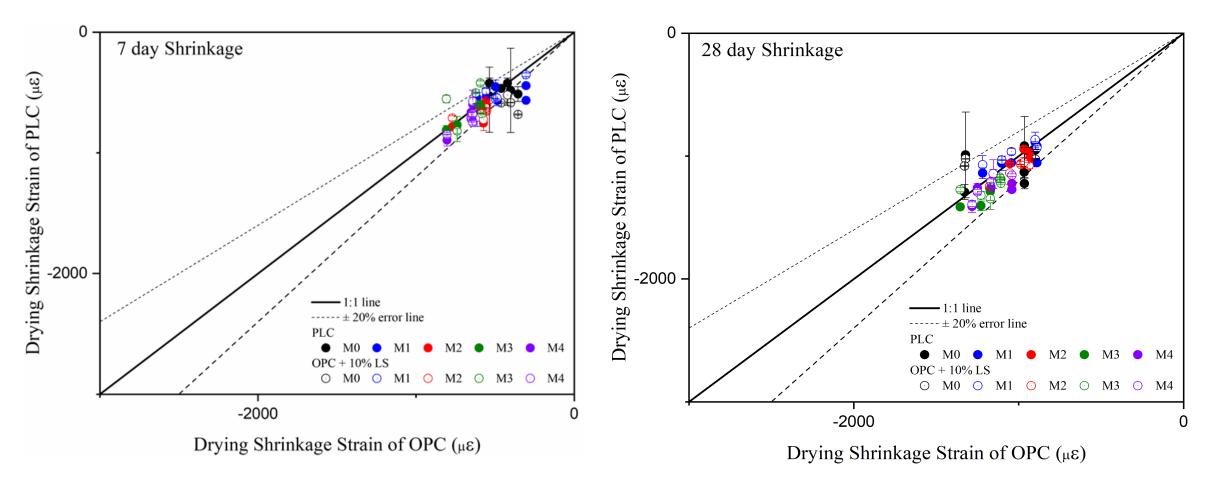
Flexural Strength at Early Ages



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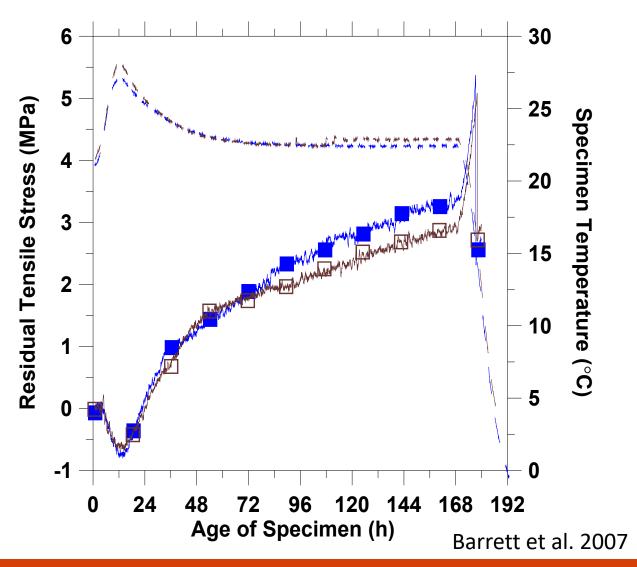
Shrinkage Behavior (Free Shrinkage)



Choudary et al. in press

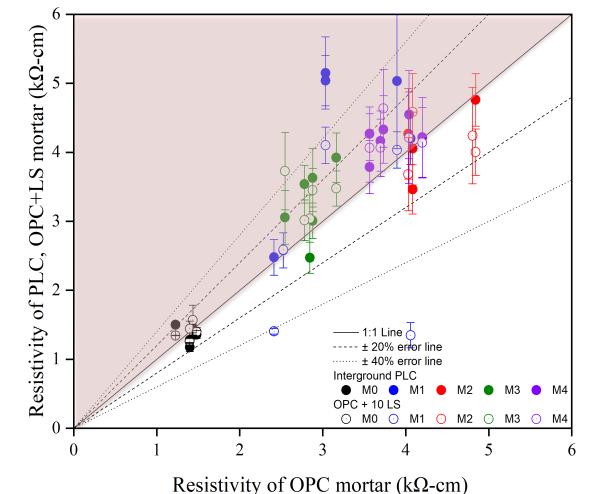
Restrained Shrinkage

- Restrained shrinkage is about more than free shrinkage
- Several tests of commercial cements were performed and, in all cases, when the samples had equivalent strength, they had similar shrinkage cracking
- Both strength and modulus play a role



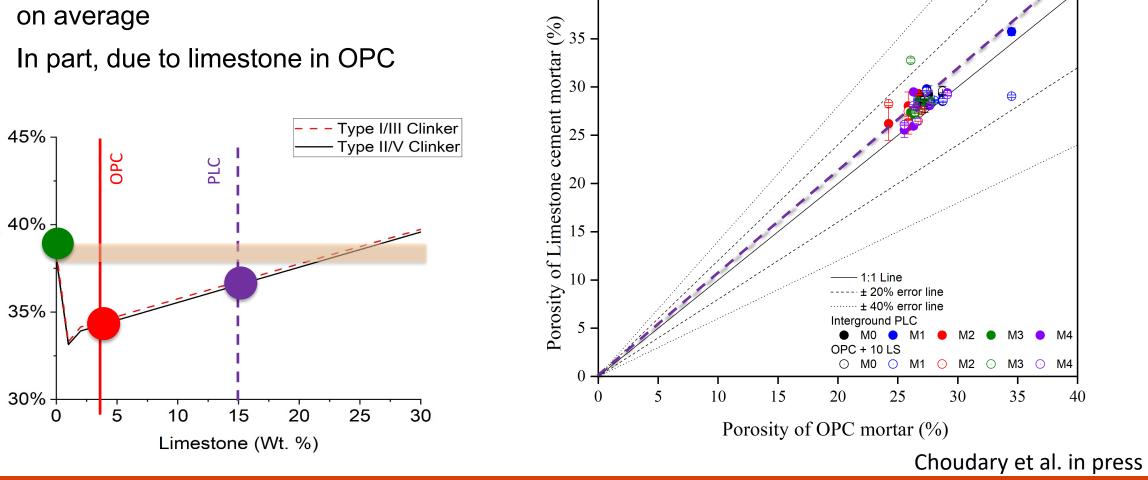
Electrical Resistivity (Similar results to RCPT)

- Higher resistivity is better (less permeable)
- First, everything with SCM is substantially better than the plain OPC
- Second, the vast majority of PLC-SCM mixtures are above the average line (PLC outperforms OPC)
- Third, the one exception is some of the fly as mixtures (especially with separately added limestone)
- In the literature some are 'a lot better' some are 'a little lower' ... lets discuss why



Pore Volume

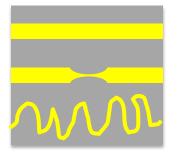
- A 3% increase in pore volume is noted • on average
- In part, due to limestone in OPC ۲



40

Porosity

Connectivity

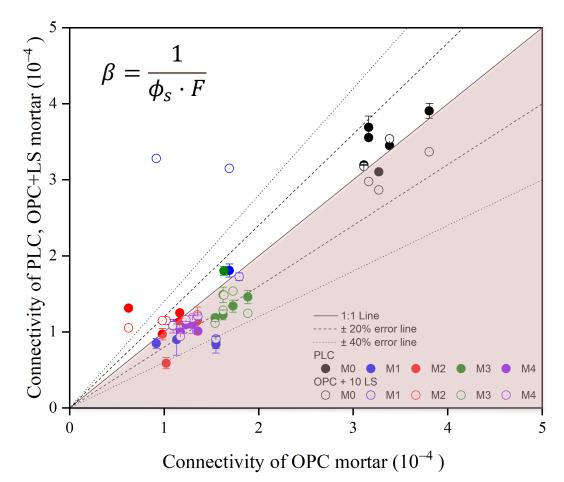


Constriction

 $\beta = 1$

Path

- One reason for the higher resistivity and formation factor even though the porosity is higher is reduced connectivity
- 2 things to notice
- SCM reduces connectivity by half
- Nearly all PLC mixtures have a reduced connectivity (which is good)



Other Major Findings

- As compared to OPC PLC systems had a
 - greater degree of clinker reaction,
 - similar or improved ASR performance,
 - statistically similar set times,
 - similar C_{crit} and time to corrosion initiation,
 - statistically similar bound chloride contents for most mixtures,
 - similar or slightly improved performance when exposed to sulfate
- Significant potential for greenhouse gas reduction (GHG)
 - 6.5% to 17.1% with an average of approximately 10-12%.

https://doi.org/10.5399/osu/1150



Growing concern - industrial waste, 'off-spec'

ENVIRONMENT NEWS

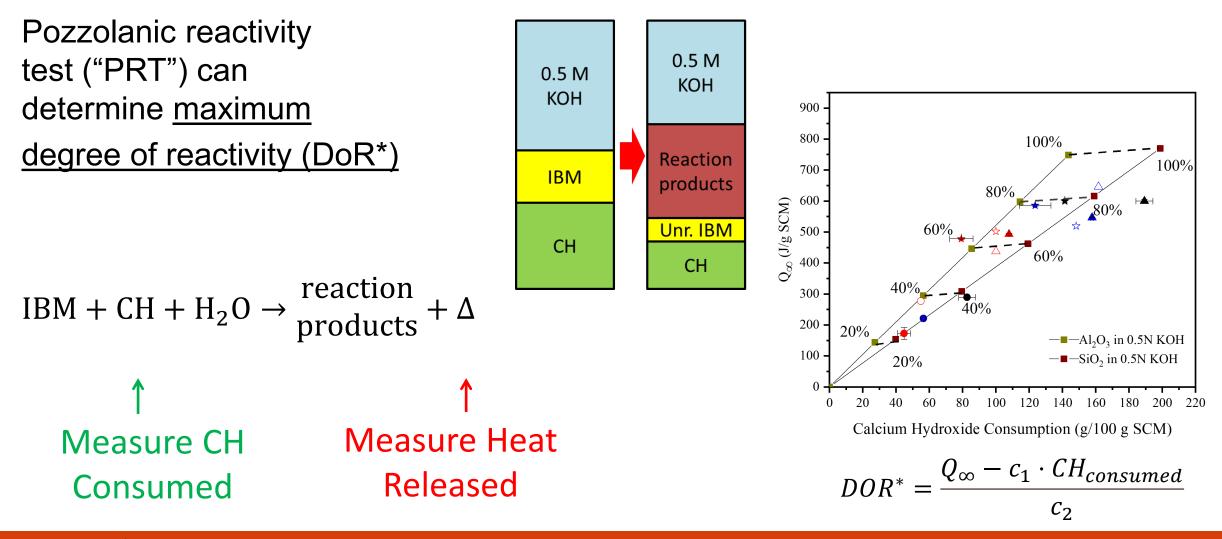
Coal's other dark side: Toxic ash that can poison water and people

Workers who cleaned up a huge spill from a coal ash pond in Tennessee in 2008 are still suffering—and dying. The U.S. has 1,400 ash dumps.



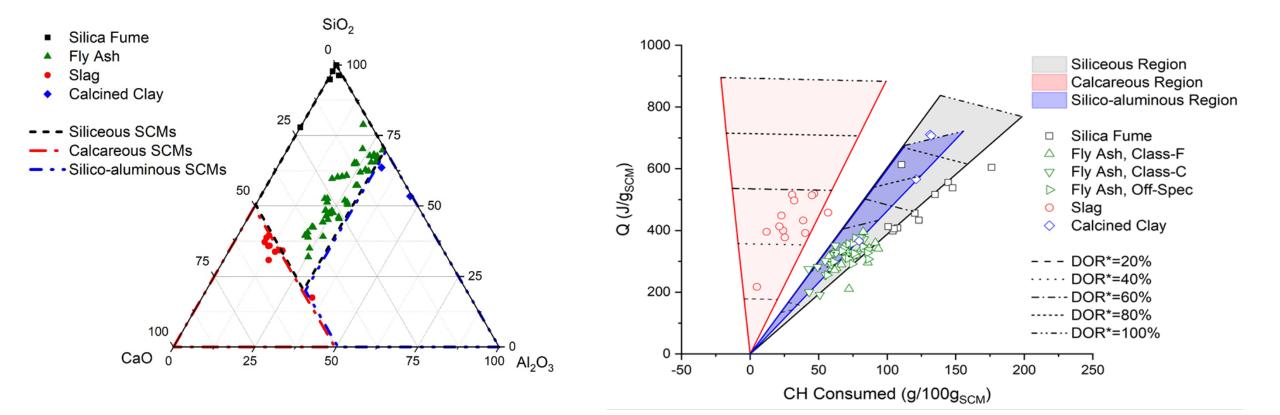
NATIONAL GEOGRAPHIC

Pozzolanic reactivity test (PRT)



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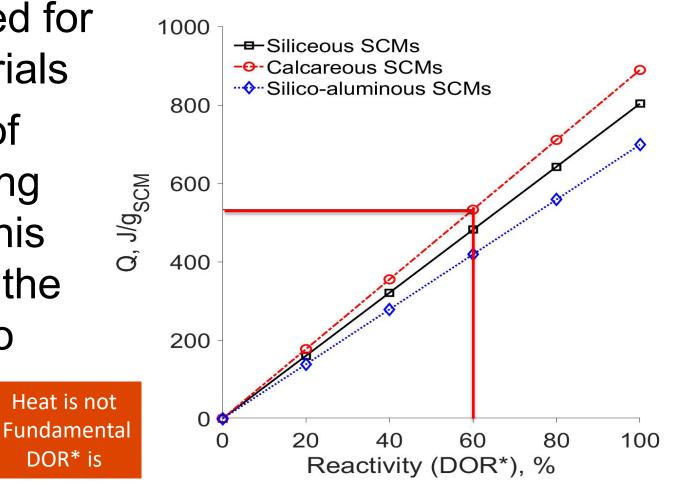
Commercial SCMs



Bharadwaj et al. 2021

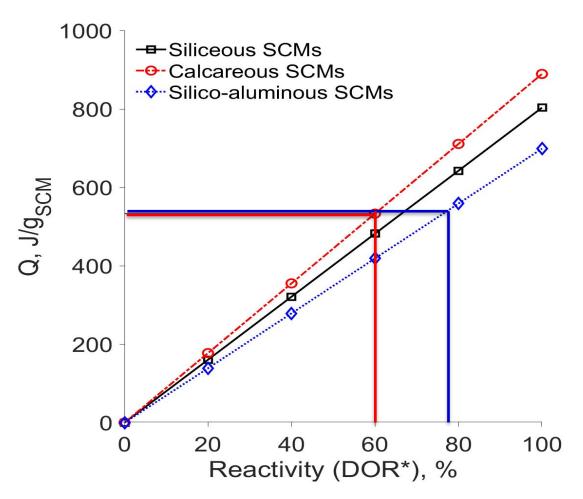
PRT Simplification

- Since the Q/CH is fixed for a given class of materials
- If we know the class of material we are working with we can simplify this approach and rely on the use of one measure to obtain DOR*

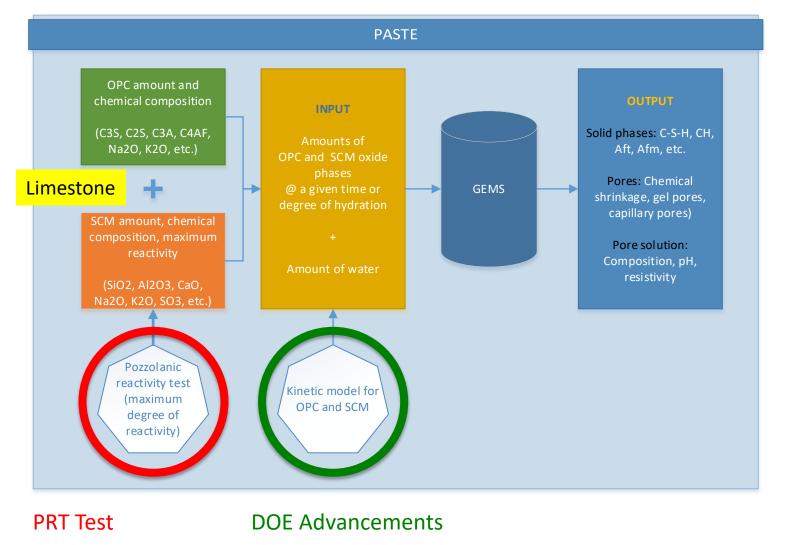


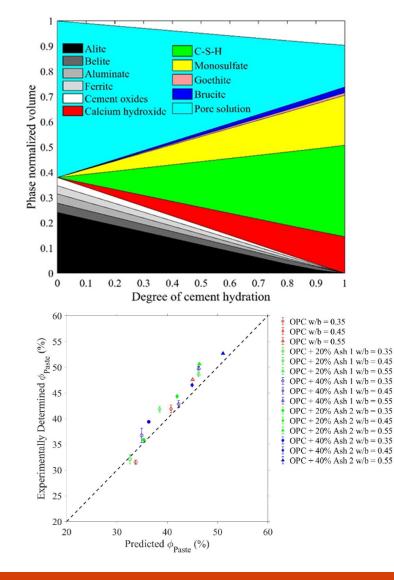
PRT Simplification

- Since the Q/CH is fixed for a given class of materials
- If we know the class of material we are working with we can simplify this approach and rely on the use of one measure to obtain DOR*



New Approach to Mixture Design Development





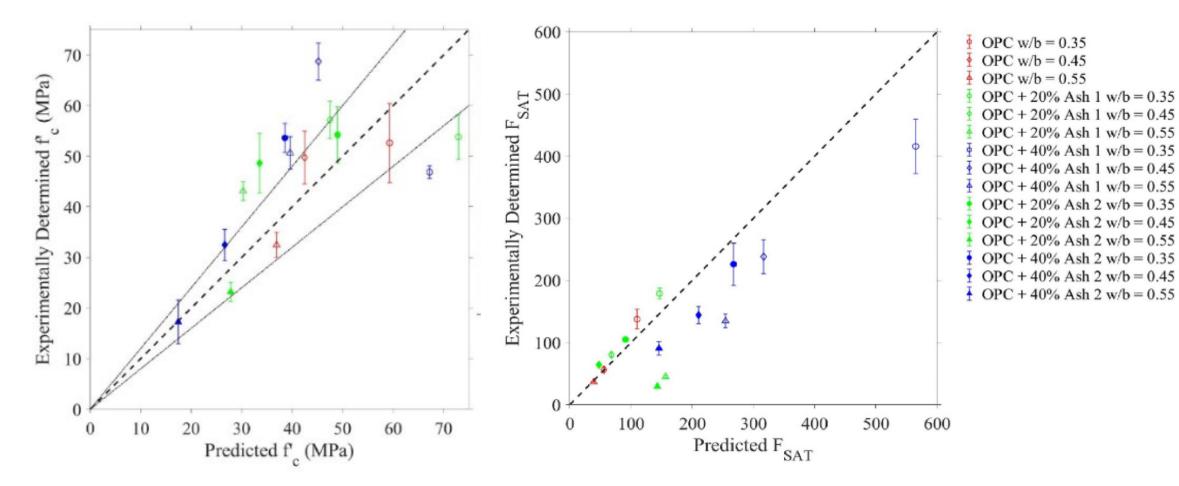
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Modeling Predictions (Off Spec/Reclaimed/Bottom Ash)

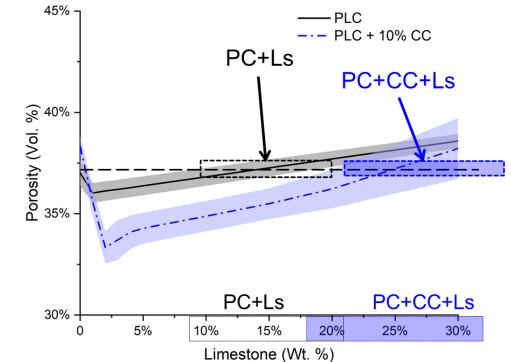
Compressive Strength

Formation Factor



Explore New Compositions

PLC + Al₂O₃: Porosity (%) SCM Replacement (Wt.% of Binder) ¹⁰ 01 01 02 05 05 ¹⁰ 01 01 02 05 ¹⁰ 01 02 05 ¹⁰ 01 02 05 ¹⁰ 01 02 05 ¹⁰ 01 05 ¹⁰ 05 45 40 20 ŝ 5 35 20 ¢ na 38 30 Bharadwaj et al. 2021 30 33 34 35 36 25 25 0 20 30 10 0 Limestone Content in PLC (Wt.%)



Bharadwaj et al. 2020

Proportioning Mixtures to Better Utilize SCMs and Reduce Cement

Current approaches do not utilize the specific chemistry of the SCM nor do they consider durability aspects in the design

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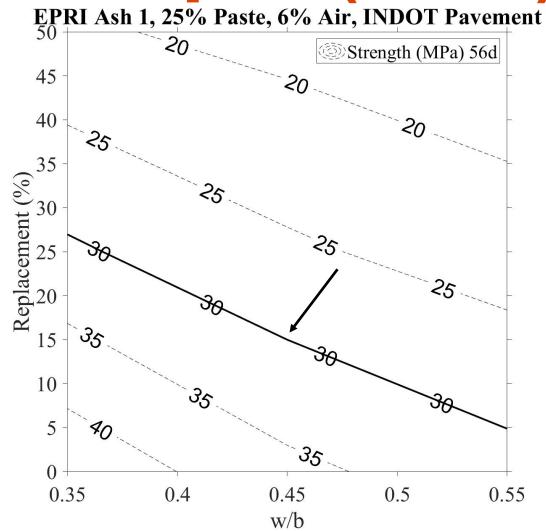
Design Example

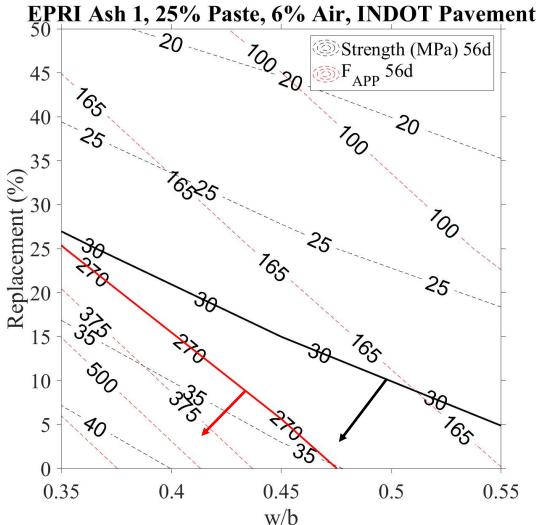
Midwest pavement (no reinforcement) with resistance to CaOxy and freeze-thaw damage



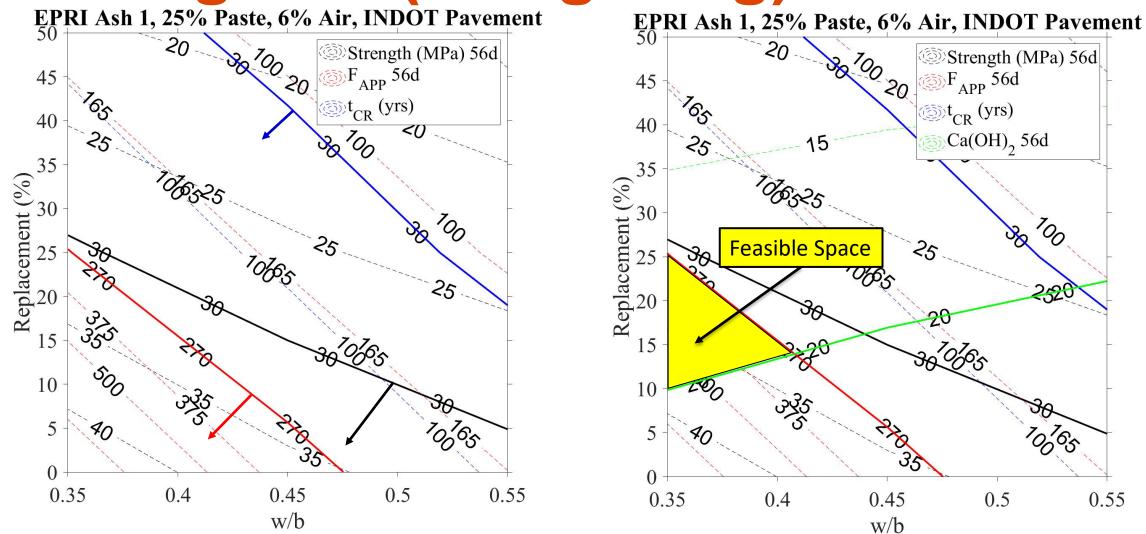
PRT Test DOE Advancements

Strength (> 29 MPa) Transport (> 270)





Freeze-Thaw (30 years) Deicing Salt (<20 g/100g)



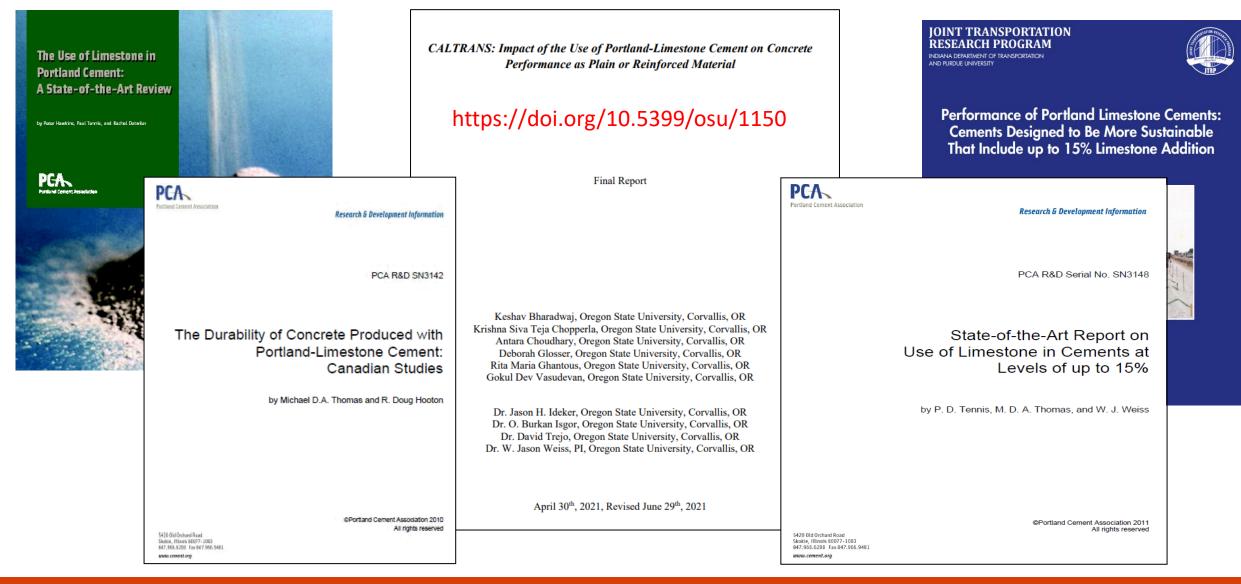
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0.55

Summary

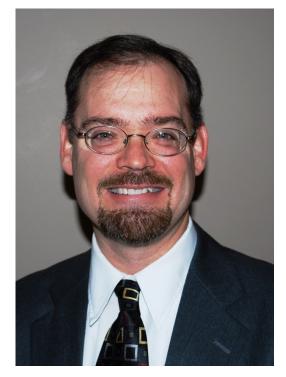
- Cement production results in CO₂ release
- Many innovations are discussed but we need innovations at scale that are ready to use
- Today we talked about
 - Portland Limestone Cement Its ready lets use it
 - Pozzolanic Reactivity Test (PRT) It can be used to quantify performance both commercial and emerging SCMs
 - Computational tools enable mixtures to be simulated not just trial and error which can greatly accelerate change

Other References



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Today's Panelists



Moderator: Paul Tennis



R. Doug Hooton, University of Toronto



Jason Weiss





America's Cement Manufacturers™

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