Decreasing the Clinker Component in Cementing Materials: Performance of Portland-Limestone Cements in Concrete in Combination with Supplementary Cementing Materials

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Why Portland-Limestone Cements (PLC)?

- Portland Cement manufacturing produces CO_2
  - Limestone decomposition
  - Fuel consumption
- Governments are preparing cap and trade limits on point source CO_2 emissions
- Not new since PLC (CEM IIA-L) has been in use in Europe for > 20 years and is now the most widely used cement type

PLC in Canadian Standards

- In 2008, a new class of Portland-Limestone cements was added to the cement standard, CSA A3001, with up to 15% blended or interground limestone replacing cement clinker.
- The CO_2 emissions from PLC are ~10% less relative to CSA Type GU (~ASTM Type I) Portland cement.
- 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.
- PLC have to meet the same set time and strength development performance as portland cement of the same type (eg. GU ---same as ASTM Type I)

Portland-Limestone Cements in Canadian Standard

- Changes to the CSA A3000 Cementitious Materials standard in 2008 and to the A23.1 Concrete standard in 2009 allow use of PLC
- The National Building Code of Canada was updated in 2010 to include these changes

More Sustainable Cementing Materials

SCMs (and blended cements)

PLC

Portland cement type	Blended hydraulic cement type	Portland-limestone cement type
GU	**GUb** **(GULb)**	**GUL**

CSA A23.1 Types of Hydraulic Cements

Portland cement	Blended hydraulic cement	Portland-limestone cement ***	Name
GU	GUb	GUL	General use cement
MS	MSb	-	Moderate sulphate-resistant cement
MH	MHb	MHL	Moderate heat of hydration cement
HE	HEb	HEL	High early-strength cement
LH	LHb	LHL	Low heat of hydration cement
HS	HSb	-	High sulphate-resistant cement

*** Portland-limestone cements shall not be used in sulphate exposures as defined in Table 3 of CAN/CSA-A23.1 (even when mixed with SCMs)

PLC in Sulfate Exposures

- Currently PLC is not allowed in sulfate exposures by the CSA A23.1 concrete standard due to concern with potential for thaumasite sulfate attack (TSA) at cool temperatures (5-10 ^{o}C).
- However, in 2010, the CSA A3001 cement standard was revised to allow PLC blended cements in sulfate exposures
- Research is ongoing to develop sufficient data to revise the A23.1 concrete standard to allow PLC + SCM (or blended cements) in sulfate exposures.

Thaumasite Form of Sulfate Attack

30-year-old bridge column exposed to wet oxidized sulfide clay in England

Thaumasite is not so common, but when it occurs, it attacks the whole matrix.

Photos from UK Expert Panel

New Test for Evaluating Mitigation of Thaumasite Sulfate Attack

- A new test method, based on ASTM C1012, but with mortar bars stored in sulfate solution at 5 ^{o}C, was standardized by CSA in 2010
- In this new test, PLCs were found to show potential to form thaumasite, if used as the sole binder.
- But when sufficient levels of slag, fly ash, metakaolin, and silica fume (ternary) binders were used, no thaumasite formed.
- This was the basis for CSA A3001 being revised in 2010, allowing blended cements with limestone

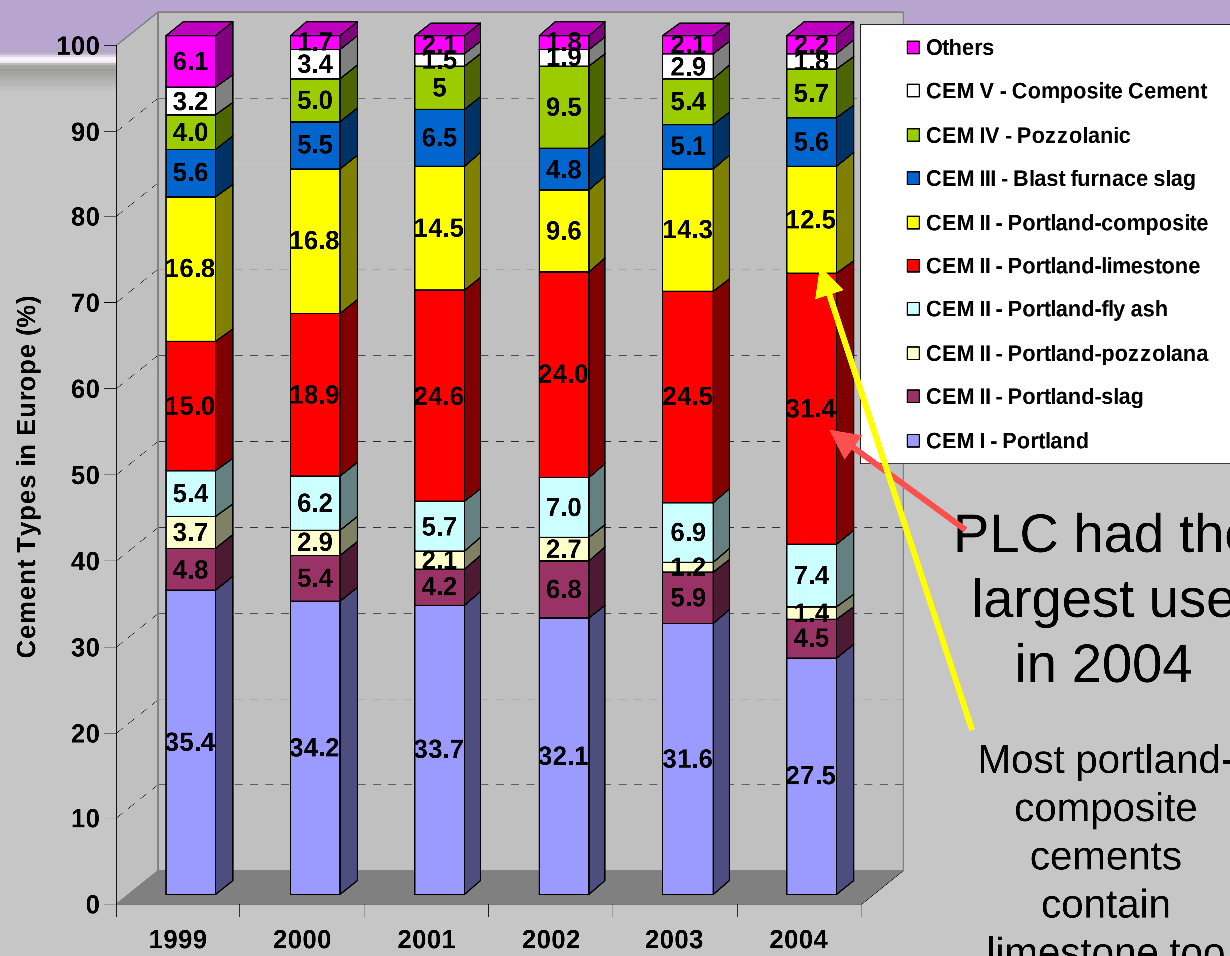
ASTM and PLC

- At least 2 producers in the USA are making 10% limestone cements under ASTM C1157 and have used them in both structures and pavements.
- ASTM C595 may be amended in 2011 to allow for PLC blended cements.
- In support of ASTM activities, Thomas & Hooton prepared a report: PCA R&D SN3142, *The Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies.*

A3001 PLC Performance Requirements

- In CSA A3000, the setting times and strength development limits are the same for PLC as for portland cements.
- Heat of hydration limits are also the same for MH and LH cements.
- In concrete, PLC also performs well with slag or fly ash at normal replacement levels.
- Mechanisms: Carbo-aluminate hydrates form and also fine carbonates provide nucleation sites that accelerate hydration

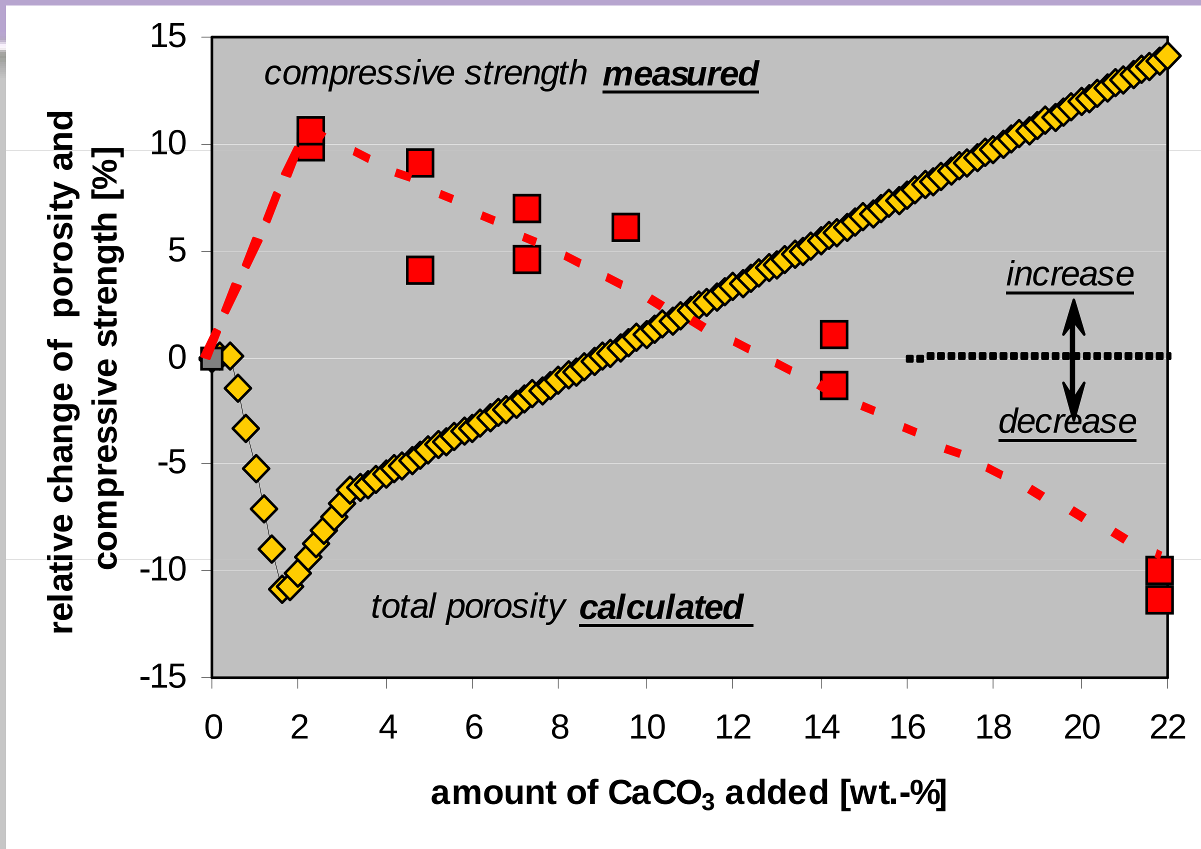
Cement types sold in Europe 1999 - 2004 (according to Cembureau data)



PLC had the largest use in 2004

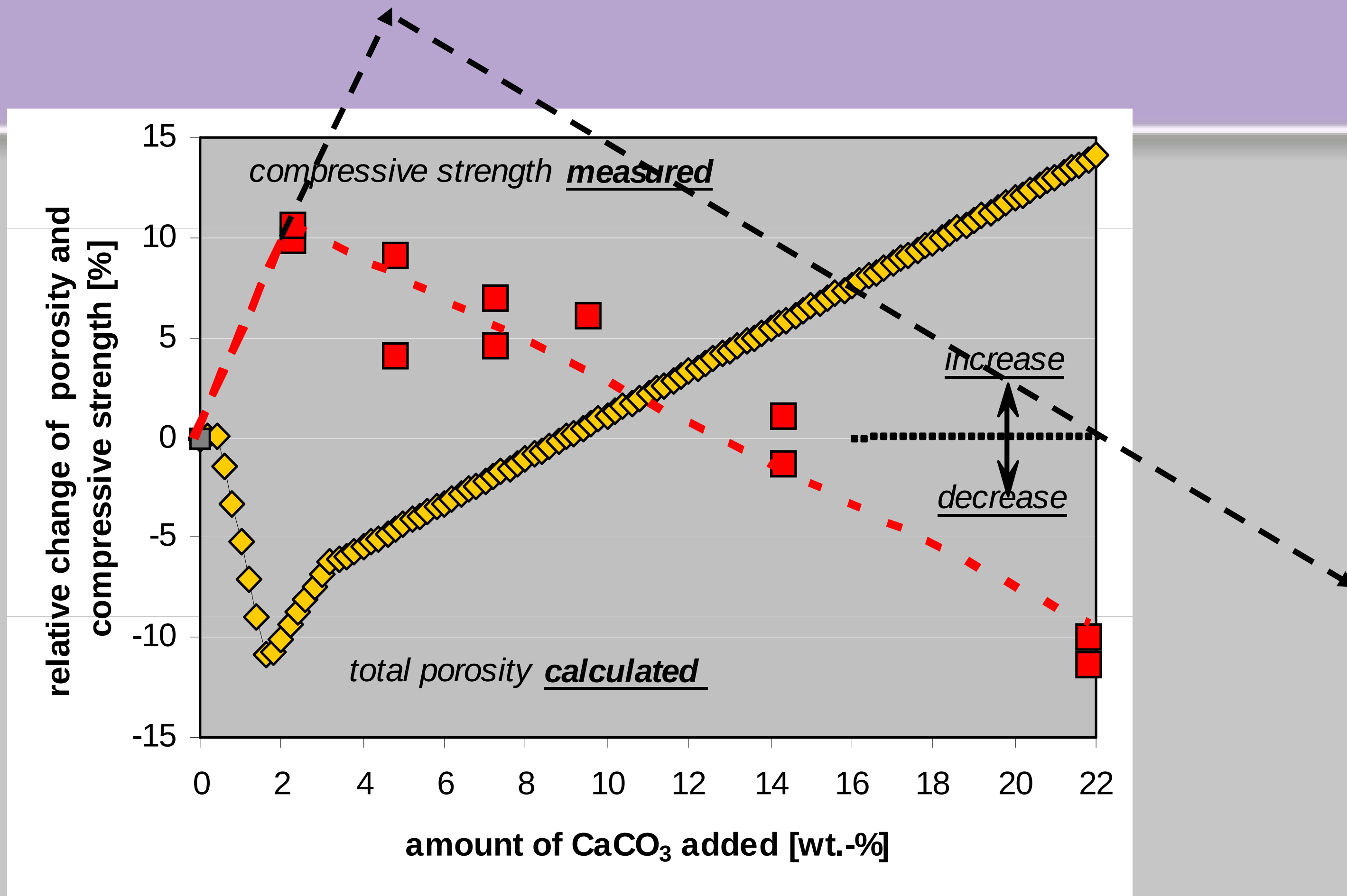
Most portland-composite cements contain limestone too

Why PLC works: (Herfort, 2008) Limestone and cement aluminates form Carboaluminates, which fill in porosity and increase strength + if get more aluminates from SCM, optimum will shift to higher % limestone



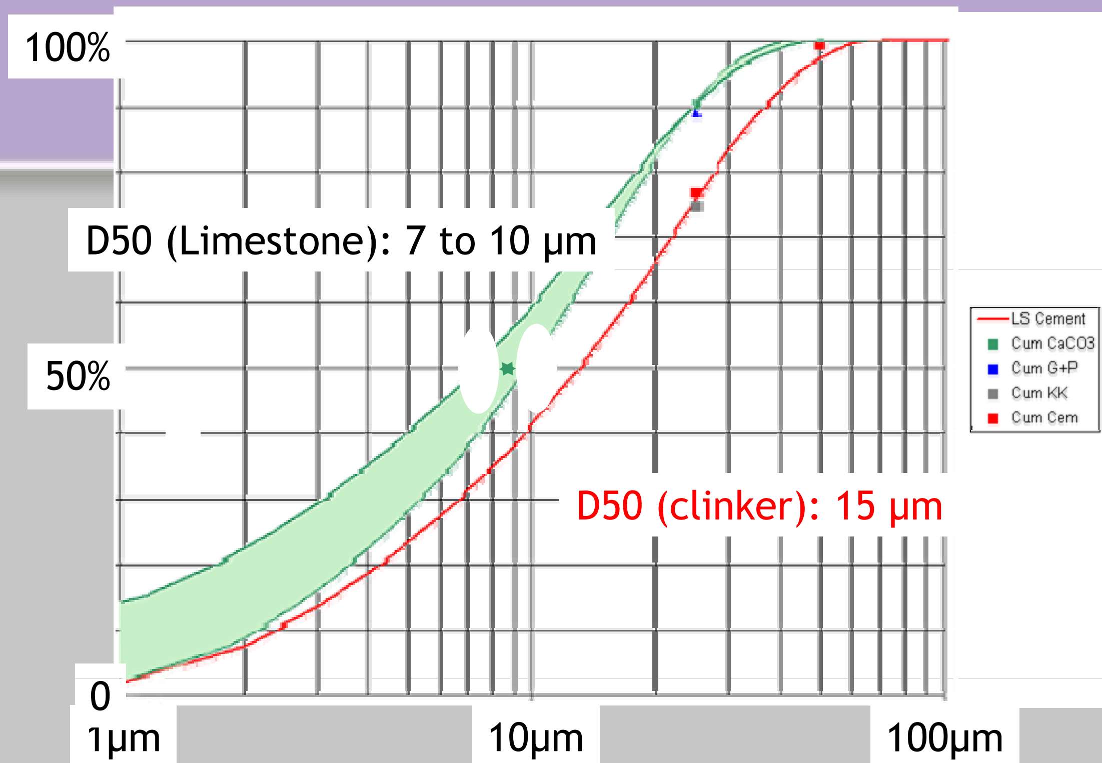
Equal strength at 0 and 13% PLC

PLC + Slag, Fly Ash, or Metakaolin



Research is currently underway at U of Toronto to confirm

Limestone Fineness



Limestone fineness in the interground product is significantly finer than the clinker fraction

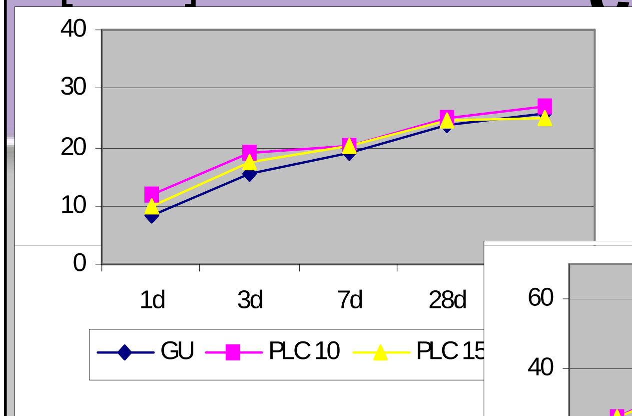
L. Barcelo, Lafarge

Lab Concrete Data

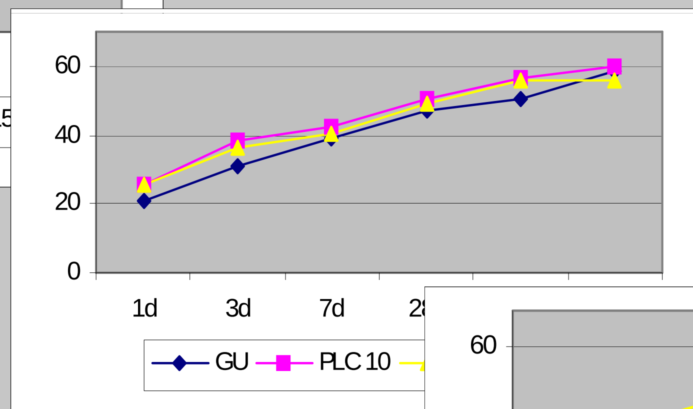
- Before balloted by CSA A23.1, all of the Cement companies and several universities performed extensive testing for fresh, hardened, and durability properties on PLC and together with SCMs normally used.
- A couple of examples follow.

Initial concrete test results – **straight cement (and limestone)**

[MPa]



w/c 0.70



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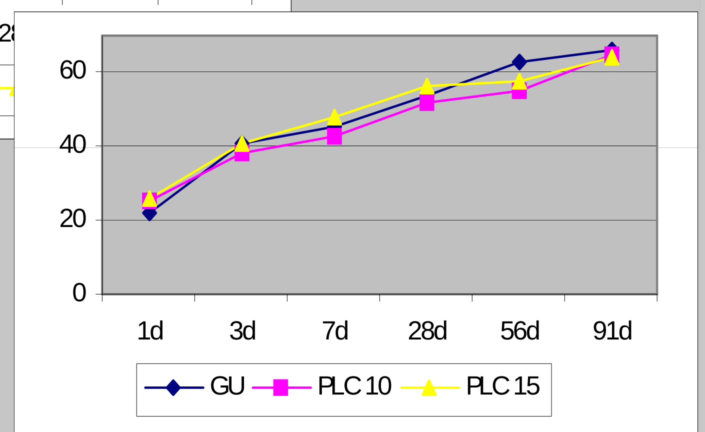


w/c 0.37

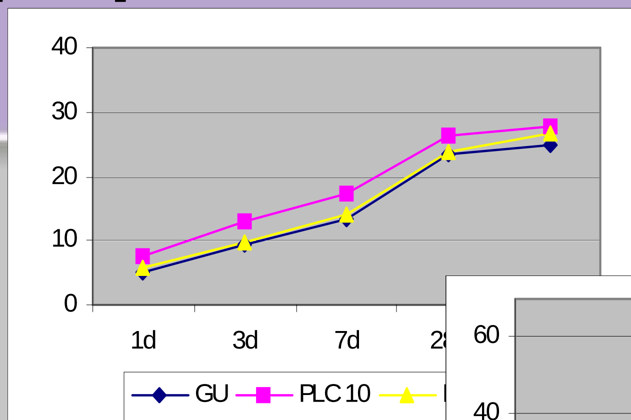
GU

PLC10

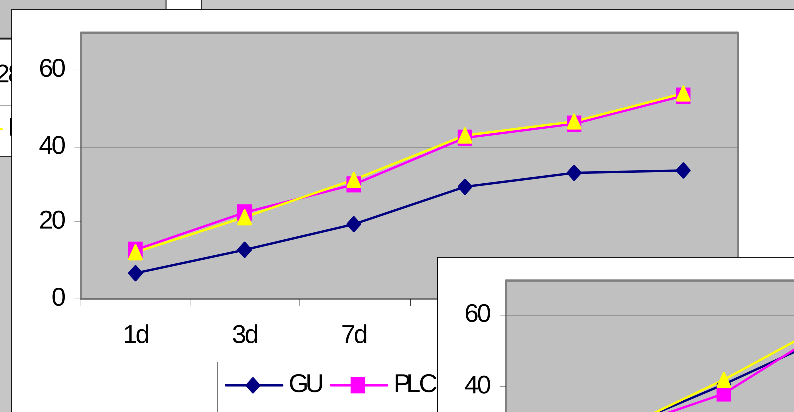
PLC15

Initial concrete test results – **with 30% Slag**

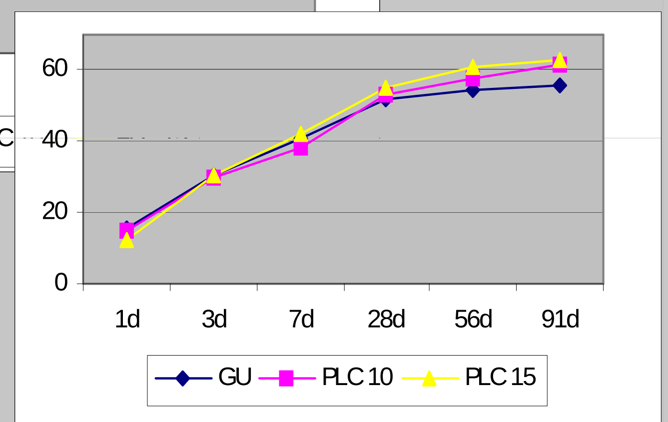
[MPa]



w/cm 0.70



w/cm 0.40



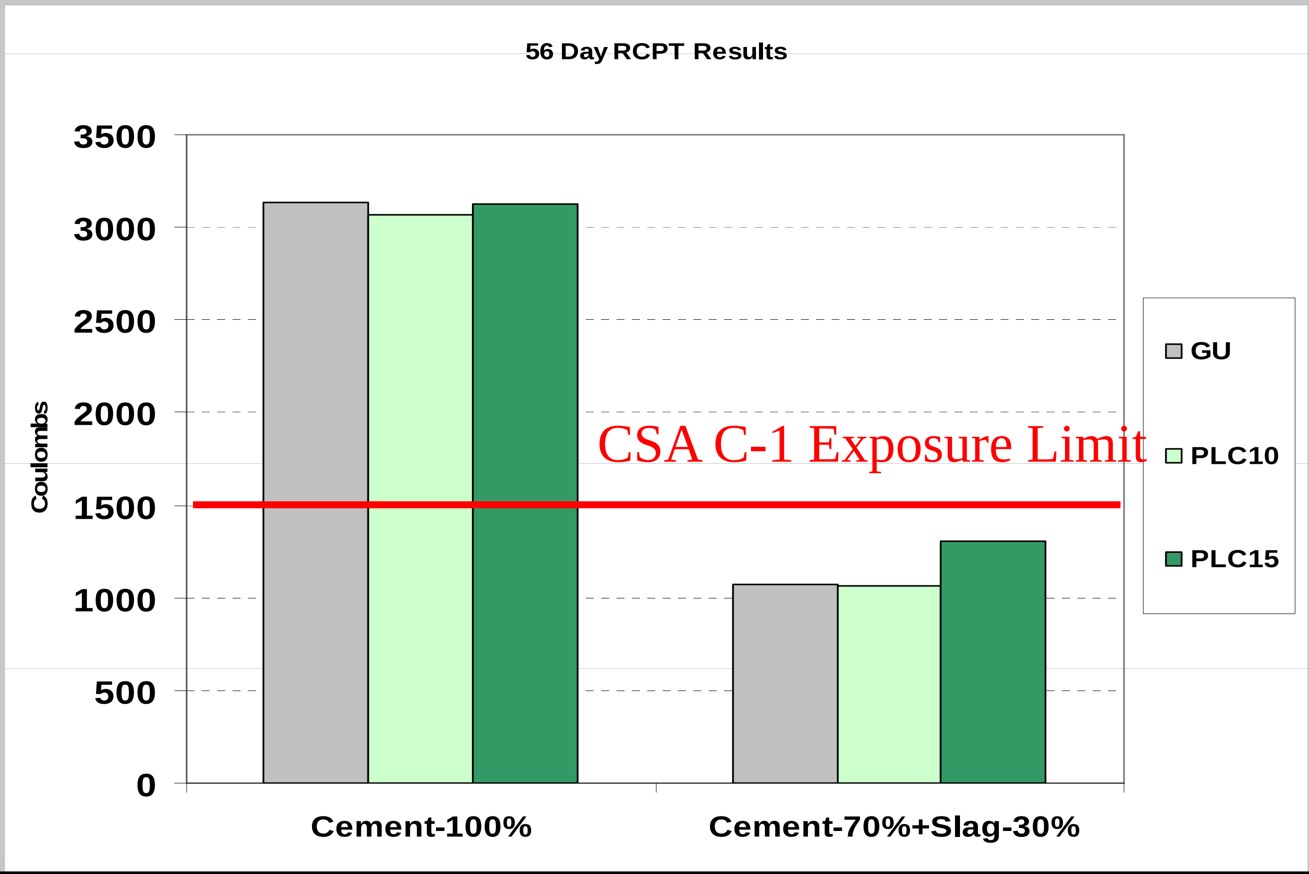
w/cm 0.37

GU

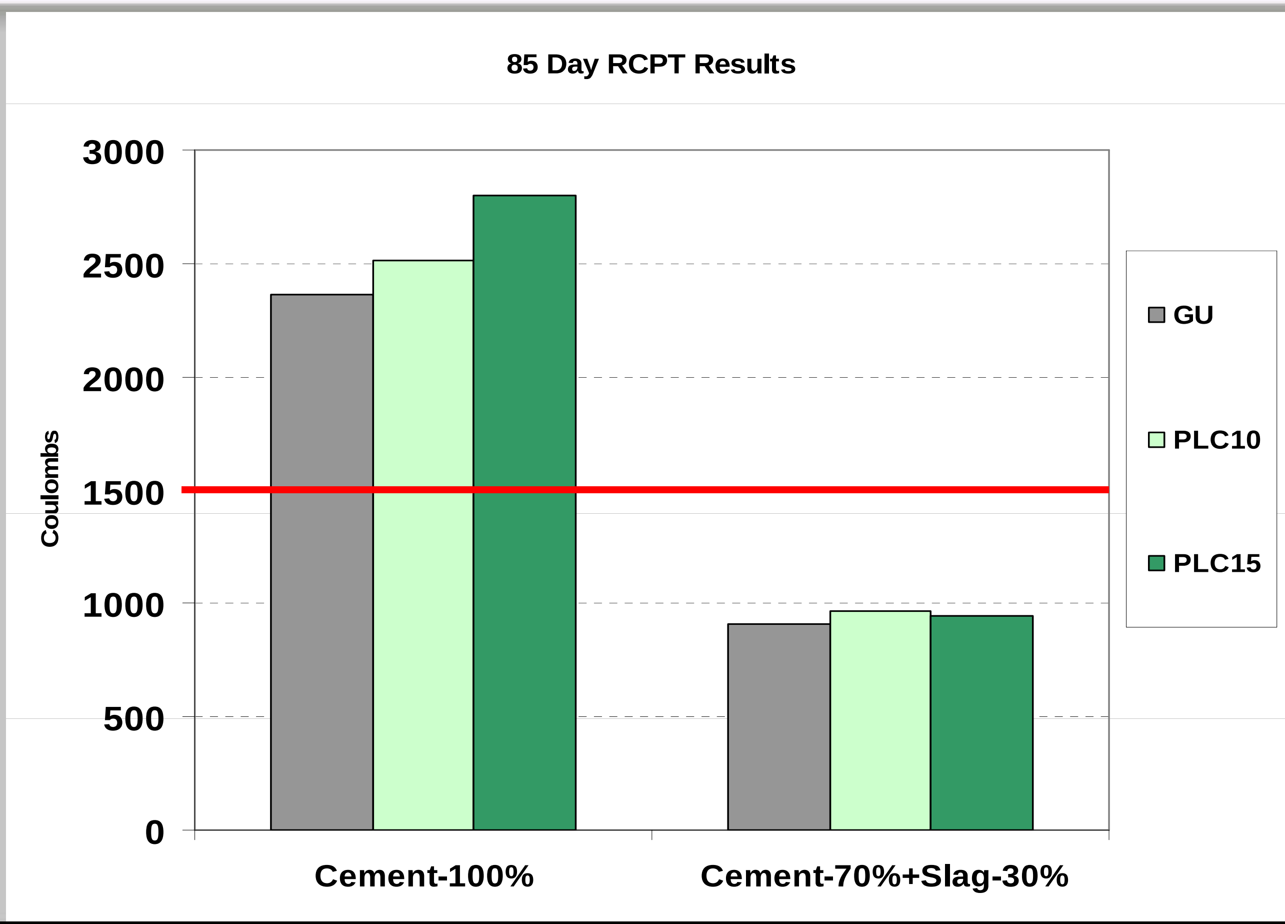
PLC10

PLC15

56-day ASTM C1202 Results (w/cm = 0.40)



85-day ASTM C1202 Results

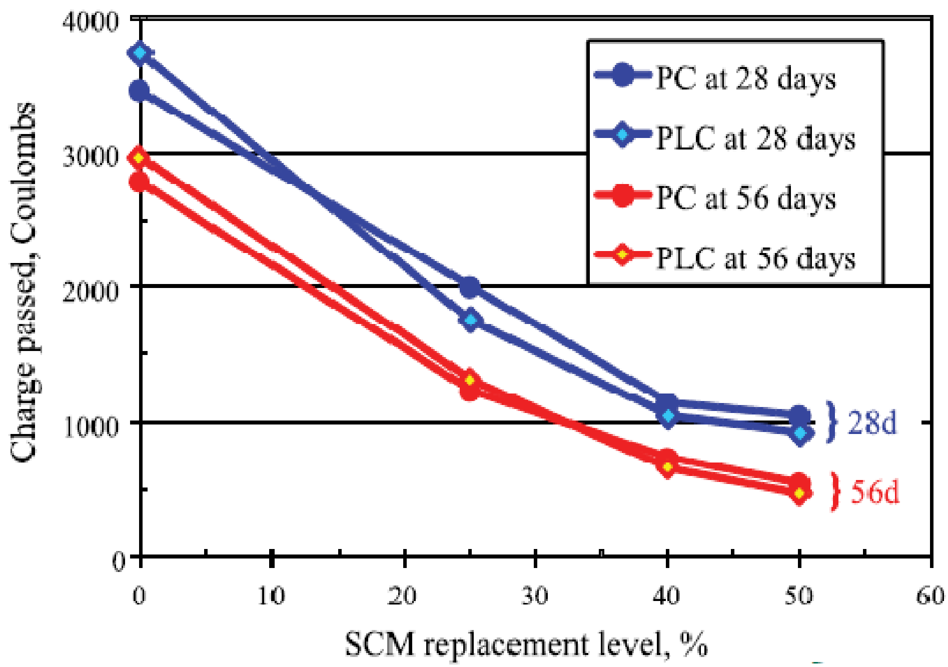


Lafarge PLC Trials from 2008 (Concrete International Jan 2010)

BY MICHAEL D.A. THOMAS, DOUG HOOTON, KEVIN CAIL, BRENTON A. SMITH, JOHN DE WAL, AND KENNETH G. KAZANIS

- 8 concrete slabs were cast in Oct 2008 at Lafarge, Gatineau QC
- 80-100mm (3-4 in.) slump, air-entrained, 30MPa, C-2 exposure(355kg/m3, 592 pcy)
- GU and PLC with 0, 25, 40 & 50% mixed SCM (2 slag: 1 fly ash)

RCP Coulomb Values for Site Cast Cylinders & Cores



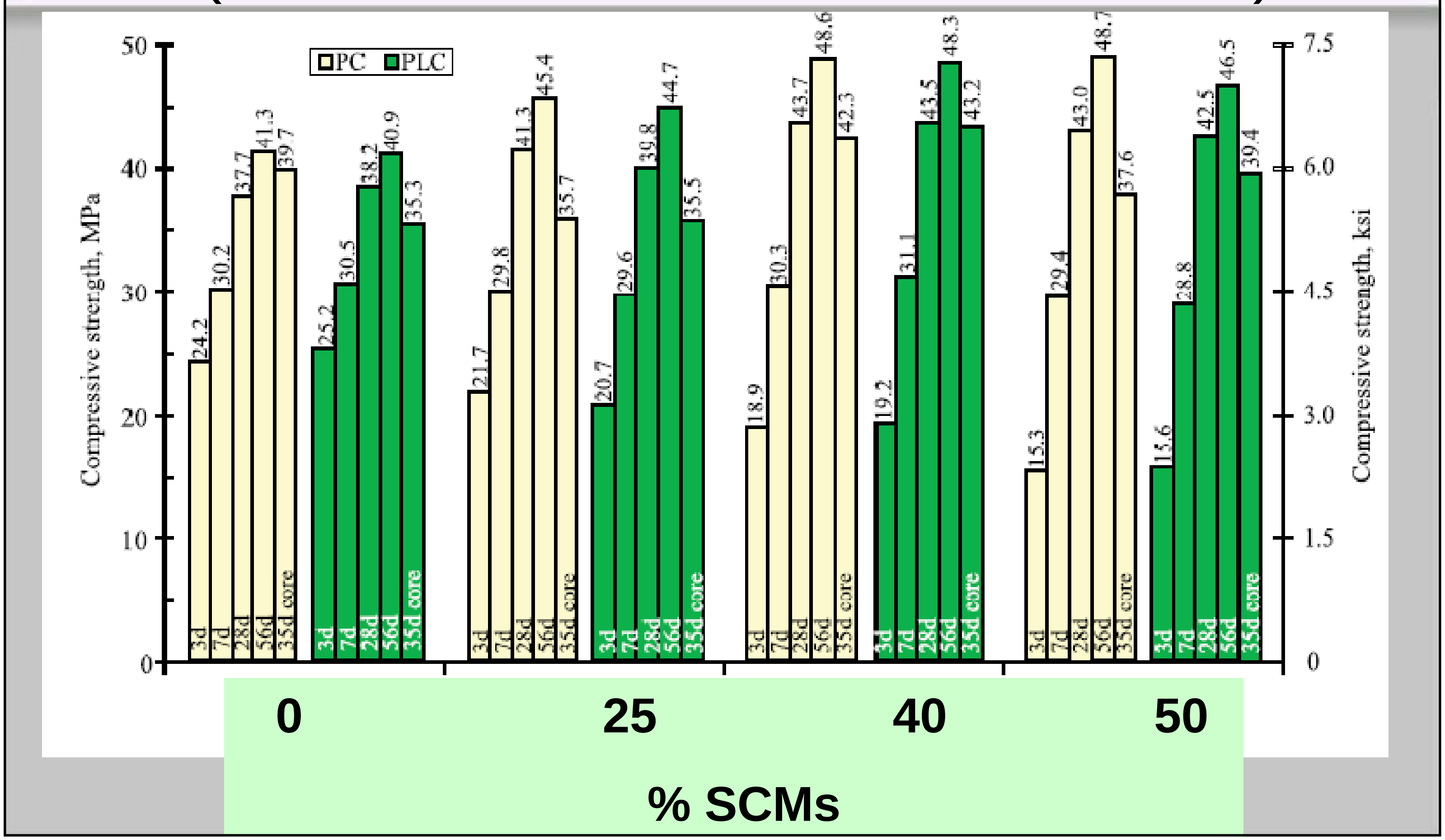
Equal performance of GU and PLC mixes at same age and SCM content

RAPID CHLORIDE PERMEABILITY TEST (ASTM C1012) RESULTS FOR CORES TAKEN FROM SLABS AT 35 DAYS (VALUES IN COULOMBS)

Cement type	SCM replacement level, %			
	0	25	40	50
PC	2400	1410	570	490
PLC	2350	1310	620	520

3, 7, 28, 35-day Cylinder & 35-day Core Strengths

(12% limestone PLC mixes in Green)



Air Void, Freeze/Thaw and Chloride Diffusion Data

AIR VOID PARAMETERS PER ASTM C457 AND DURABILITY FACTOR (RESISTANCE TO FREEZING AND THAWING) PER ASTM C666

SCM replacement level, %	Cement type	Air void parameters		Durability factor, %
		Air content, %	Spacing factor, µm	
0	PC	5.3	173	101
	PLC	5.6	187	100
25	PC	4.9	148	101
	PLC	5.4	149	104
40	PC	5.6	164	101
	PLC	5.3	165	103
50	PC	5.6	150	102
	PLC	6.6	147	100

TABLE 5:
CALCULATED VALUES OF DIFFUSION COEFFICIENT D_A ($\times 10^{-12}$ m^2/s) FROM BULK DIFFUSION TESTS PER ASTM C1556

Cement type	SCM replacement level, %			
	0	25	40	50
PC	15.0	3.8	1.5	1.3
PLC	11.9	2.9	1.2	1.8

Nov. 2009 Barrier Wall

- Dufferin Construction Barrier Wall Test sections 23m^3 of PLC+Slag vs GU+Slag
- Queen Elizabeth Expressway in Burlington
- First MTO trial of PLC
- Testing performed by Dufferin Concrete (Holcim) and University of Toronto.

PLC Barrier Walls on QEW
Nov. 4, 2009

GU Cement + 25% Slag

GUL Cement + 25% Slag

23 m^3 of each mix was placed, 30 MPa, 60-100 mm (2.5-4 in.) slump

Nov. 2009 QEW Barrier Wall

QEW Barrier Wall	PC +25% SLAG	PLC + 25% 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/m^2**	**0.24 kg/m^2**
RCP (Coulombs)		
28 days	**2070**	**1490**
56 days	**1930**	**1340**

PLC Paving Trial Sept 27, 2010

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

- New Highway 401 East bound exit to #10 from collector lanes.
- 100 m of paving was done with PLC+25% Slag as binder, otherwise identical to GU+25% Slag control mixture.
- Pavement was 4.25 m (13 ft) wide x 280 mm (11.5 in.) thick with pre-placed dowel baskets
- ~8 m (25 ft) was wet-cured and rest used normal curing compound

Testing

- fresh concrete tests and strength development
- Flexural and tensile strengths
- Shrinkage
- Freeze/Thaw and De-icer scaling tests
- Chloride Permeability and Bulk Diffusion
- Temperature monitoring

Concrete Plant

PLC (GUL) Test Section

Floating and Tyning

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

GUL Mix on left and GU Mix on right in Paver (note segregation in GU Mix)

Burlap & Plastic vs Curing Compound

PLC pavement at 2 months, prior to opening to traffic

7 & 28-Day Data (random samples from trucks)

	GU Control	PLC
Slump (mm)	35	20
Air (%)	5.4	4.6
Temp. (ºC)	18	19
Strength (MPa)		
7 day	35.0	31.9
28 day	50.4	48.9
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

Holcim US PLC Pavements

- Holcim makes ASTM C1157 cements with 10% limestone for use in Colorado and Utah.
- These have been used on at least 5 State paving contracts.
- In several cases the PLC was used together with Class F fly ash

Data courtesy of Al Innis, Brooke Williams, & Tom Van Dam

Colorado 2008-2009
US HW 287 Near Lamar

- 6.5 Miles PCCP with 10% Limestone cement meeting ASTM C1157 and 20% Class F fly ash (CM = 540 pcy, 322 kg/m3) w/cm = 0.34
- 28-day flexural strength average = 695 psi (4.8 MPa)
- Contractor received quality incentive per CDOT specifications
- Concrete was placed in 100 F (38C) weather without problems

Lehigh Cement Terminal 20,000 Ton Silo, 2010

- In Leeds, Alabama
- Slip-formed silo made with PLC (10%) and 40% slag
- Three concentric silos all slip-formed
- Mix used 10% limestone blended cement meeting ASTM C1157 HE (clinker was Type II low-alkali).

Data from Gary Knight and Colleagues

80 foot (24 m) diameter x 240 feet (72 m) high

Three concentric silos

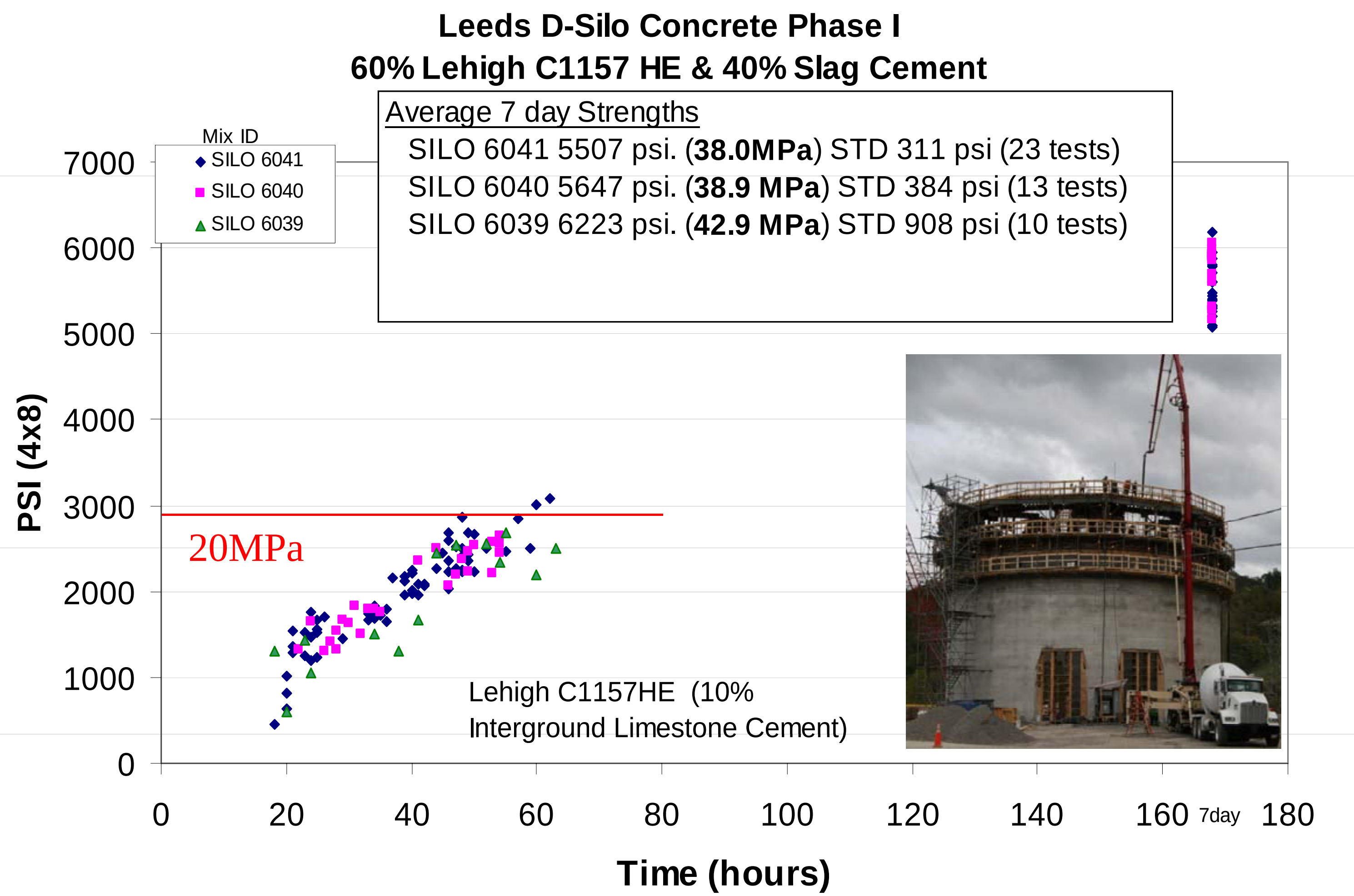
Outer wall 33 in. (0.84 m) thick at bottom

Concrete Mixture for slip Form

	PCY	kg/m3
C1157-HE PLC	420	250
Slag	280	167
Sand	1202	716
Stone	1856	1106
Water	275	164
w/cm	0.39	0.39

Water-reducer and HRWR used

Early-age and 7-Day Strengths



Summary

- Portland-Limestone cements have been used successfully in numerous pavements, in a barrier wall and in a large slip-formed silo.
- PLC works well with slag and fly ash at typical cement replacement levels.
- PLC, as defined in CSA, provides a 10% reduction in CO_2 emissions from cement plants and reduce the carbon footprint of concrete by an additional 10% without affecting performance.
- Use of PLC should not affect concrete properties or construction practices.

Portland-Limestone Cement makes "Greener" Concrete