Low-Clinker Cements: Bridging the Gap with Limestone

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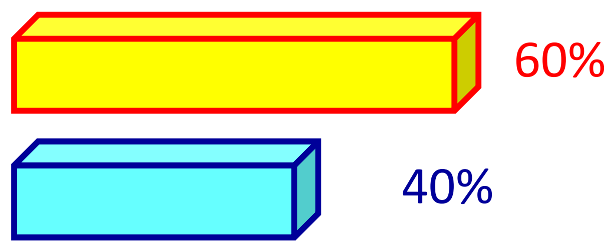
Cement production accounts for approximately 7% to 8% of CO_2 globally *(Mehta, 1998)* …

… and approximately 2.8% of CO_2 emissions in Canada *(Neitzert, 1997)*

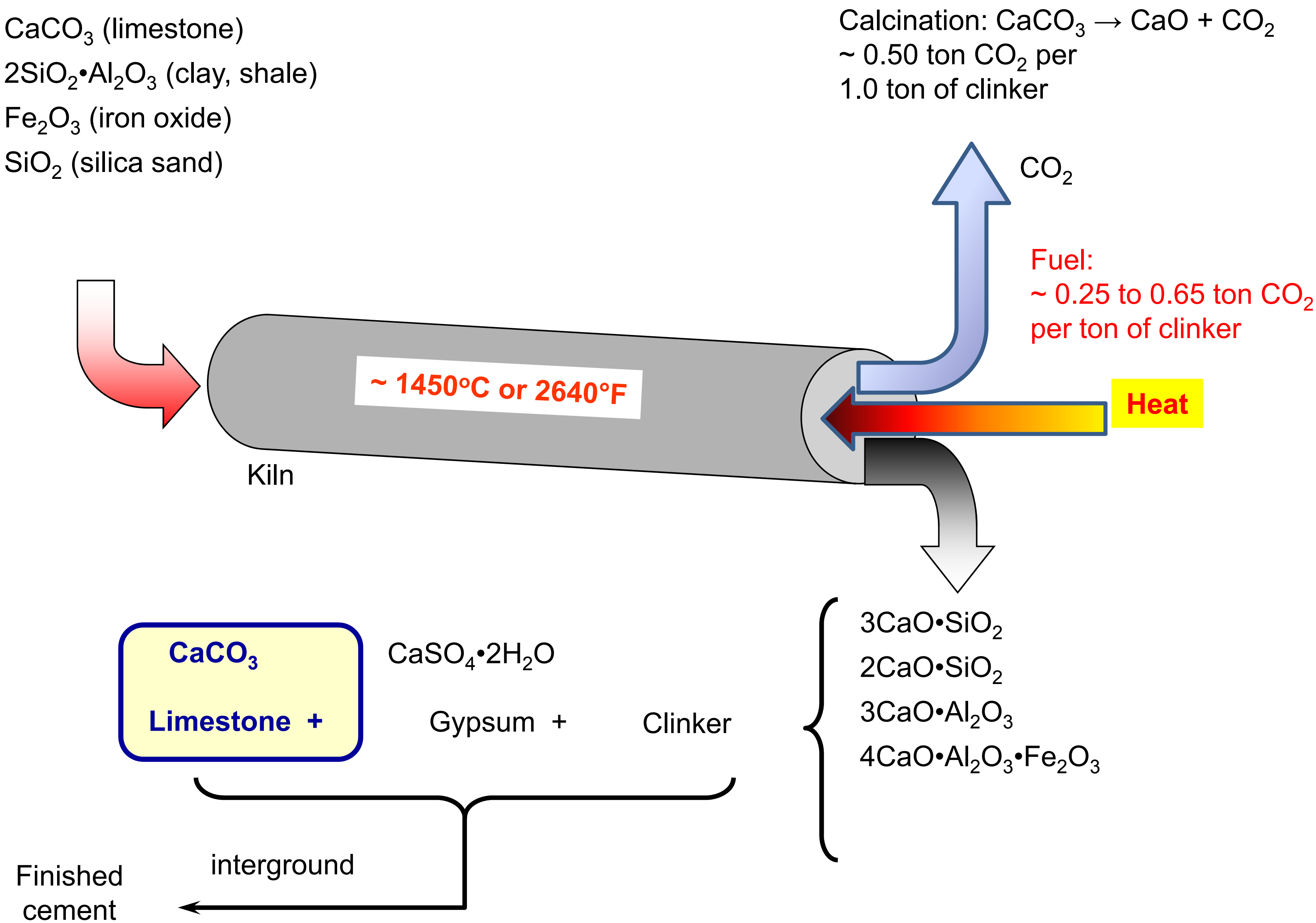
Calcination: $CaCO_3 \rightarrow CaO + CO_2 \uparrow$ (gas)

Energy: $C + O_2 \rightarrow CO_2 \uparrow$ (gas)



www.cement.ca

Portland **Limestone** Cement (PLC) Manufacture



CSA A3001-08 Types of Hydraulic Cement

Blended PLC – 2010 Amendment

New in 2008 →

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

**The suffix "b" indicates that the product is a blended hydraulic cement.*

†The suffix "L" indicates that the product is portland-limestone cement.

‡Portland-limestone cements should not be used in an environment subjected to sulphate exposure as defined in Table 3 of CAN/CSA-A23.1.

PLC is produced to provide equivalent performance to PC in Canada

So requirements for Type GUL (up to 15% limestone) same as Type GU (< 5%)

CSA A23-09 Use of Portland Cement in Concrete

- Portland limestone cement is permitted for use in all classes of concrete except for sulfate exposure classes (S-1, S-2, S-3)

Beneficial Effects of Limestone Addition

- Clinker is ground finer – leads to increased degree of hydration at any particular age
- Fine limestone particles as nucleation sites for hydration products at early hydration ages accelerating the hydration and consequently improving the early strength
- Limestone (primarily $CaCO_3$) chemically reacts with C_3A to form carboaluminates—at least at replacements of 5-10%

$$C_3A + C\overline{C} + xH \xrightarrow{hydration} C_3A \cdot C\overline{C} \cdot H_x$$

Tri-calcium aluminate in clinker

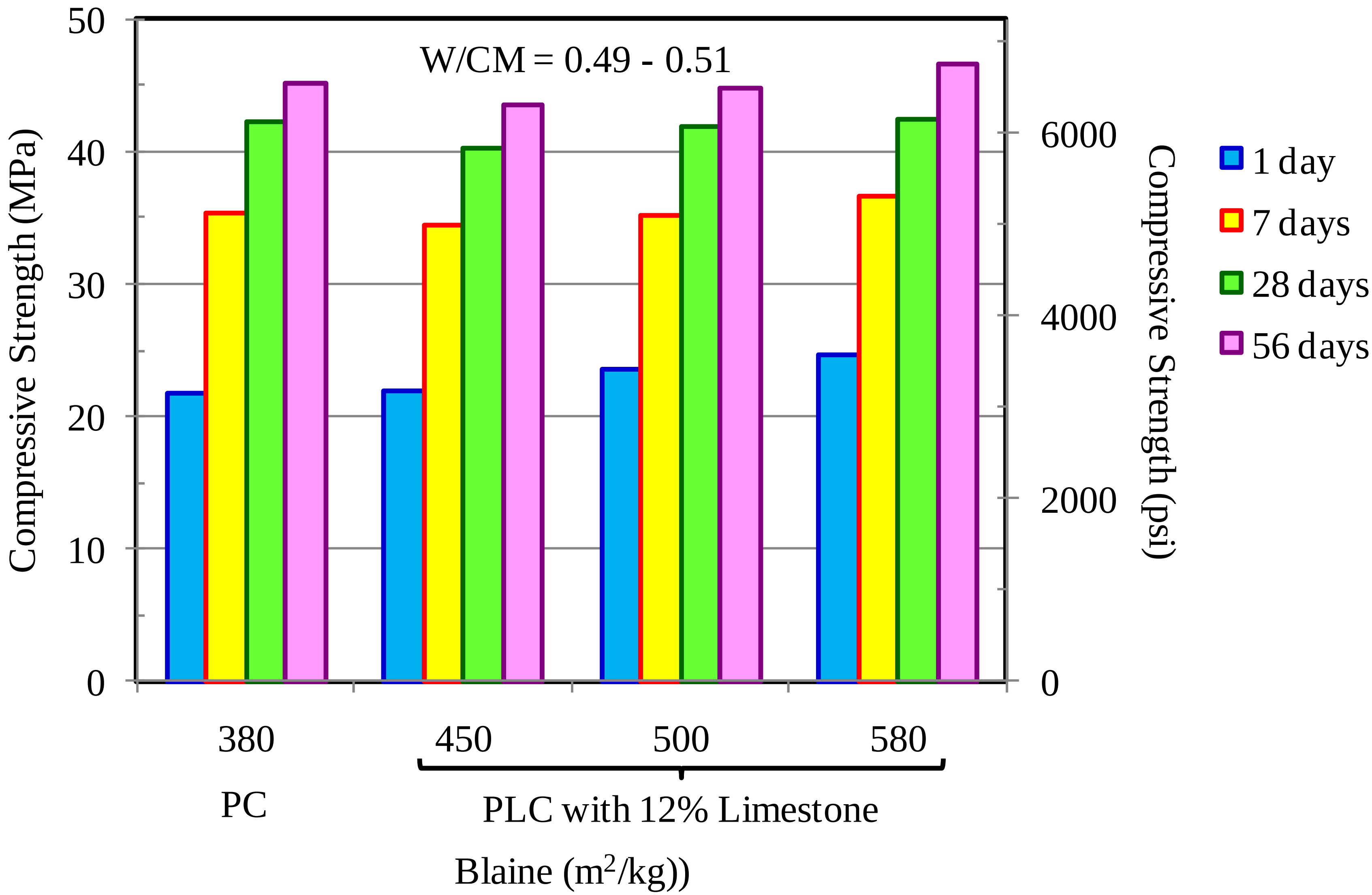
Interground limestone

Calcium monocarboaluminate (a.k.a. monocarbonate)

Limestone is not totally inert !

- Finer limestone particles fill the voids between clinker particles improving the grain packing of cement

Effect of Fineness on Performance



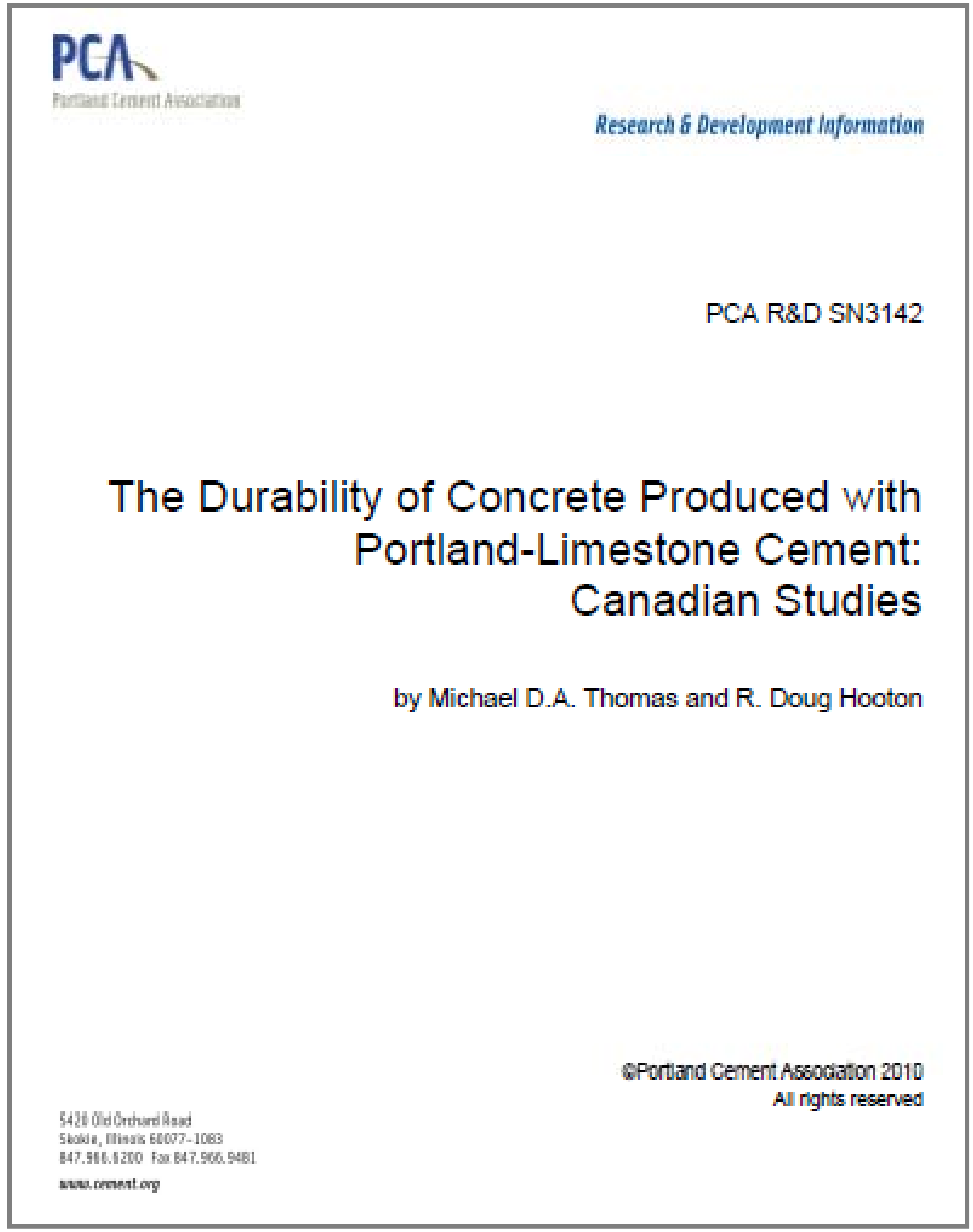
Testing in Canada indicates that the Blaine of PLC needs to be increased by approx 100 – 120 m^2/kg compared with PC to obtain equivalent performance

Tests carried out with Canadian materials: 2007-10

- Portland-limestone cements (PLC) were produced in different grinding circuits with various clinkers (C_3A from 4.5 to 12%) and limestones.
- Amount of limestone varied between 3 and 19% (to keep within limits, the real CSA PLC max. will be ~13%).
- Standard mortar tests and chemical analyses were performed on the different PLCs.
- Concrete with various w/cm ratio’s 0.35 to 0.80 were produced. The cement contents in the mixed varied between 225 and 420 kg/m^3
- Concrete tests with different PLC’s (10 to 22 %LS) and various amounts of slag (15, 25, 30%) and fly ash (20%) were performed
- Slump, slump retention and air were measured
- Durability tests were performed, e.g. RCP, freeze/thaw, salt scaling, shrinkage, sulfate resistance, and ASR
- Testing conducted by cement companies and universities
- **Field trials**

Durability of PLC Concrete: Canadian Studies

- PLC with up to 15% limestone - equivalent performance as portland cement from the same clinker
- Equivalent performance achieved by increasing Blaine by 100 to 120 m^2/kg
- Performance in this study was evaluated based on:
  - Strength
  - Resistance to freeze-thaw and de-icer salt scaling
  - “Chloride permeability” and chloride diffusion.
  - Alkali-silica reaction



PCA
Portland Cement Association

Research & Development Information

PCA R&D SN3142

The Durability of Concrete Produced with Portland-Limestone Cement: Canadian Studies

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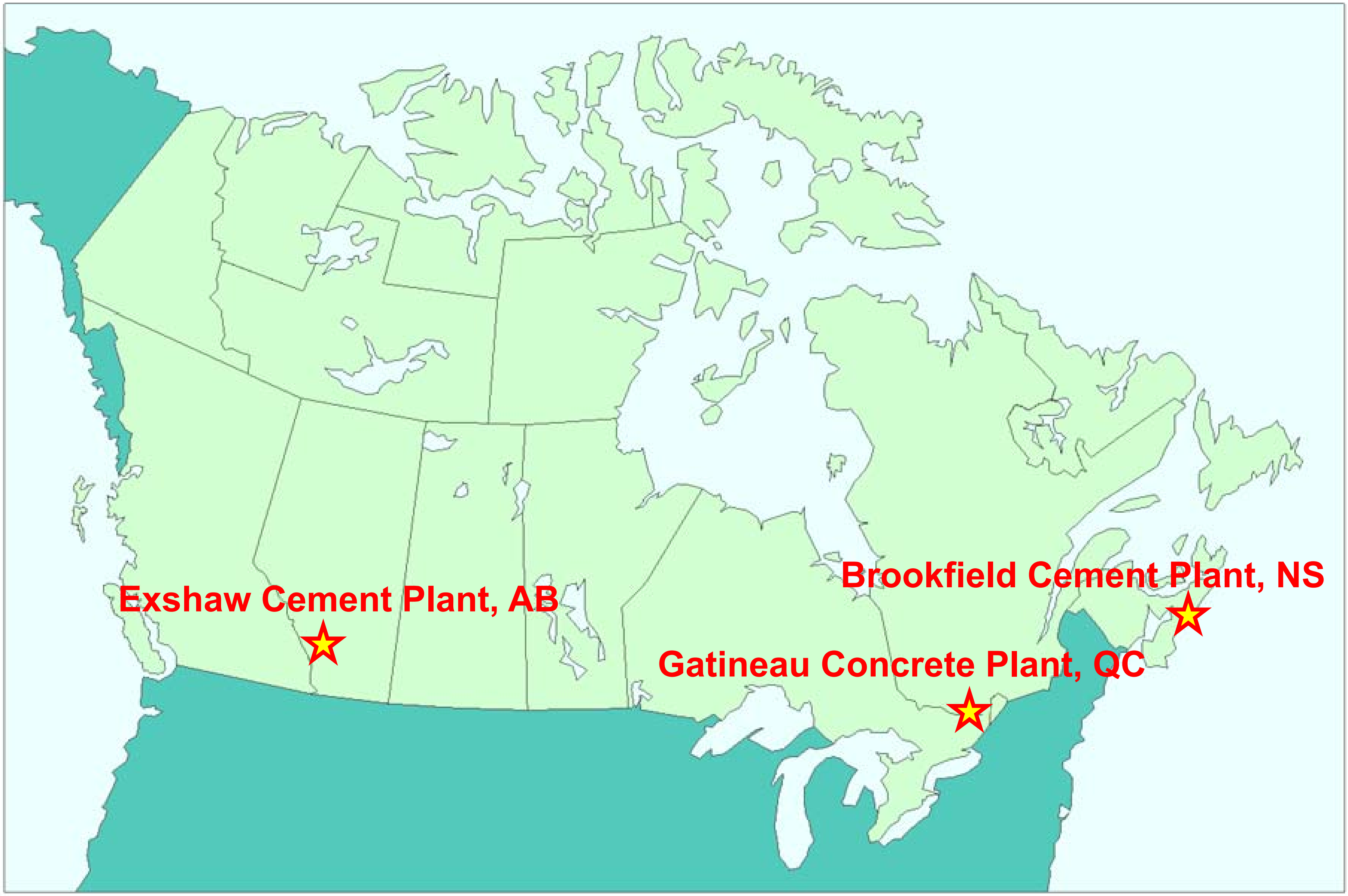
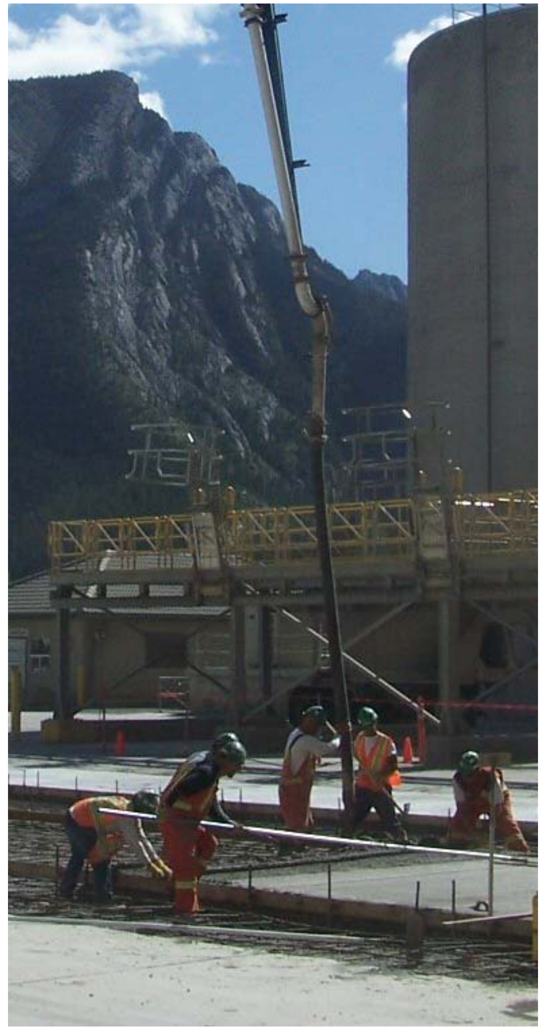
Field Trials

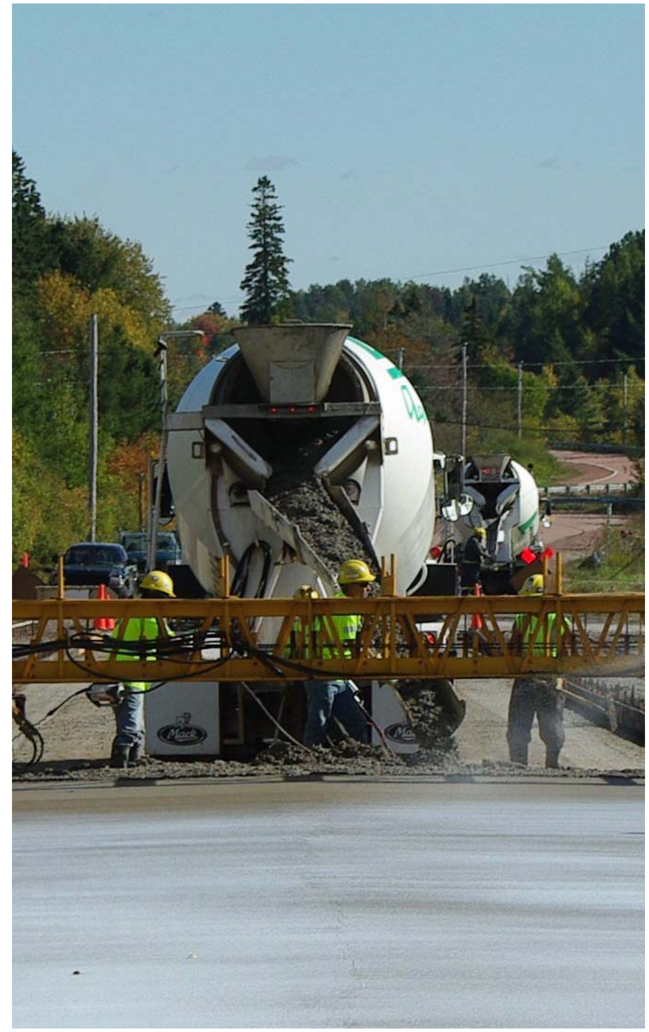


Gatineau, Quebec
October 2008

Exshaw, Alberta
September 2009



Brookfield, Nova Scotia
October 2009



Cementitious Materials used in Field Trials
CSA Terminology

CSA Type	Description	ASTM Equivalent
GU	"General Use" portland cement	ASTM C 150 Type I
GUL	"General Use" portland limestone cement	ASTM C 1157 Type GU
GUb-15S	"General Use" blended hydraulic cement	ASTM C 595 Type IS
GULb-15S	"General Use" blended limestone cement	ASTM C 1157 Type GU
F	Fly ash < 8% CaO	ASTM C 618 Class F
CI	Fly ash 8-20% CaO	ASTM C 618 Class F
S	Ground granulated blastfurnace slag	ASTM C 989

PLC Trial Pour at Gatineau Ready-Mixed Concrete Plant – October 6, 2008

Objective:

- Field test performance of PLC concrete with various levels of SCM in an exterior flatwork application.
- Control sections with Type GU + SCM

Eight Concrete Mixes:

Cement	SCM Replacement Level (%)			
	0	25	40	50
Type GU (PC)	X	X	X	X
Type GUL (PLC)	X	X	X	X

Cementing Materials:

- Type GU with 3.5% limestone (PC)
- Type GUL with 12% Limestone (PLC)
- Blended SCM = 2/3 Slag + 1/3 Fly Ash

Exshaw Cement Plant, Alberta

- Sept 2009
- Paving, Curbs & pumped concrete
- PC & PLC cements
- 15, 25 & 30% fly ash

Brookfield Cement Plant, Nova Scotia

- Oct 2009
- Paving
- Blended PC & PLC cements containing 15% slag
- 15 & 20% fly ash

	Gypsum (%)	Limestone (%)	Slag (%)	Clinker (%)	Target Blaine (m^2/kg)
Type GU	5	4	0	91	380
Type GUb	5	0	15	80	450
Type GULb	5	12	15	68	500

Brookfield Cement Plant, Nova Scotia

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Brookfield Cement Plant, Nova Scotia

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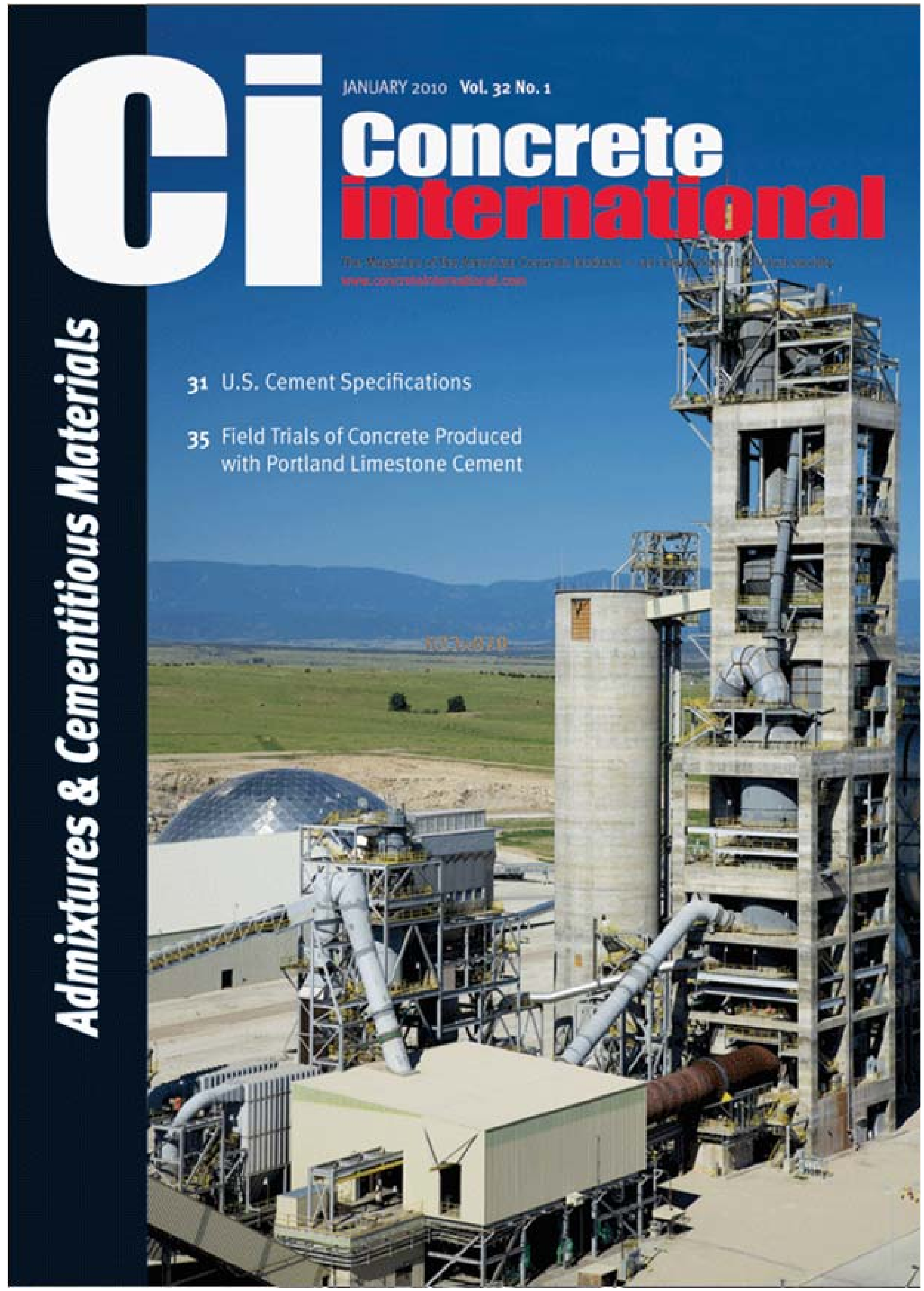
Testing of Concrete Produced for Laboratory Trials

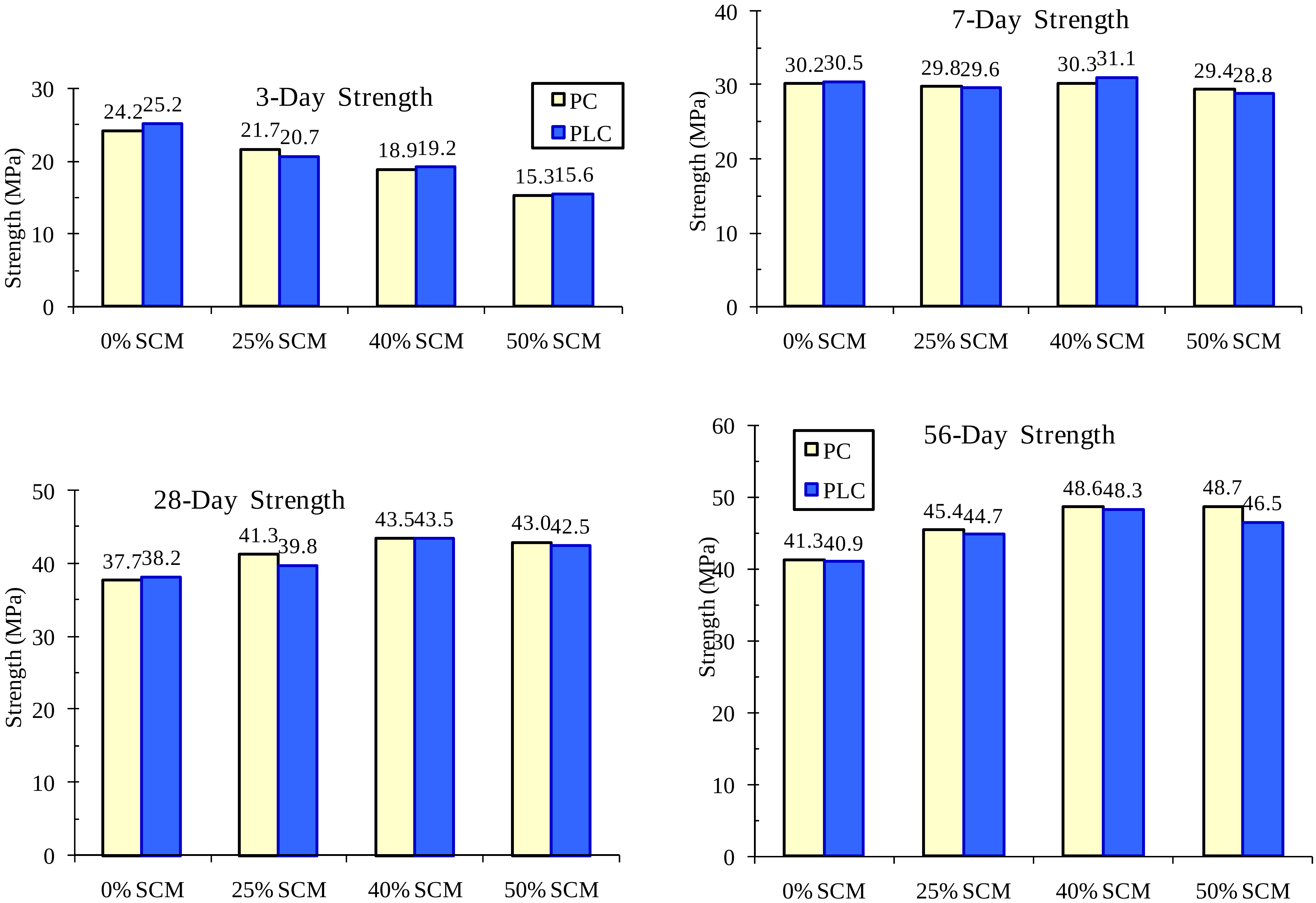
Test	Method
Slump	C 143
Air (plastic concrete)	C 231
Set time	C 403
Hardened air voids	C 457
Compressive strength	C 39
“Rapid chloride permeability”	C 1202
Freeze-thaw resistance	C 666 (Proc. A)
Salt-scaling resistance	C 672
Diffusion coefficient	C 1556

PLC Trial Pour at Gatineau Ready-Mixed Concrete Plant – October 6, 2008

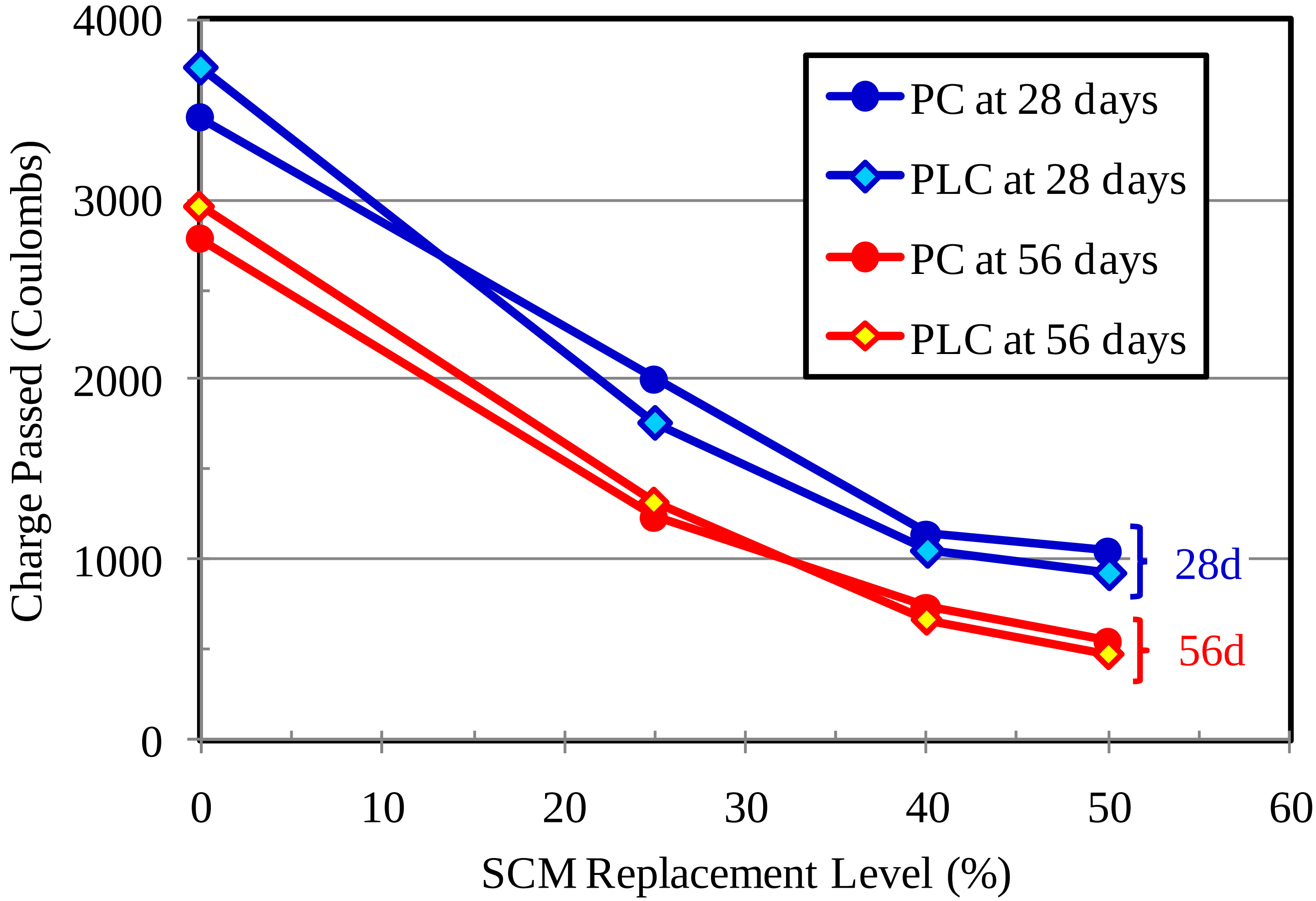
- Results published in Concrete International (Jan 2010)
- SCM had significant impact on properties
- No consistent difference between the durability results for PLC versus PC at the same level of SCM
- Mix with PLC-50% SCM contained just 42% clinker by mass of cementing material. Compare with mix with PC only – 92% clinker
- CO_2 reduced by 1 ton per 8-yd^3 truck through combined use of limestone and SCM



PLC Trial Pour at Gatineau – Cylinder Strengths



PLC Trial Pour at Gatineau – RCPT Results



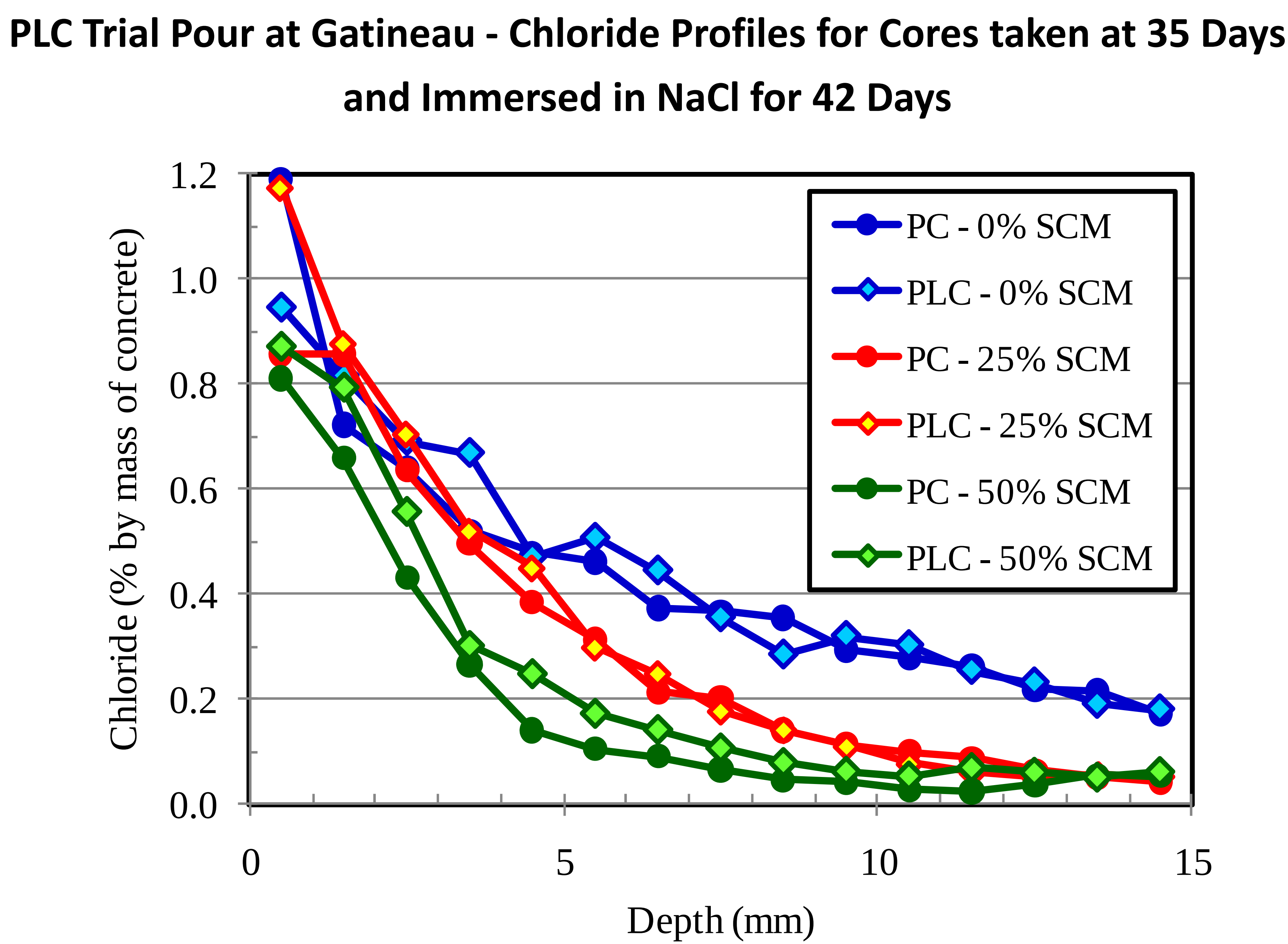
PLC Trial Pour at Gatineau – Results of Tests on Cores taken at 35 Days

RCPT Results

Cement	Charge Passed in 6 Hours (Coulombs			
	0% SCM	25% SCM	40% SCM	50% SCM
PC	2395	1410	570	491
PLC	2345	1308	617	520

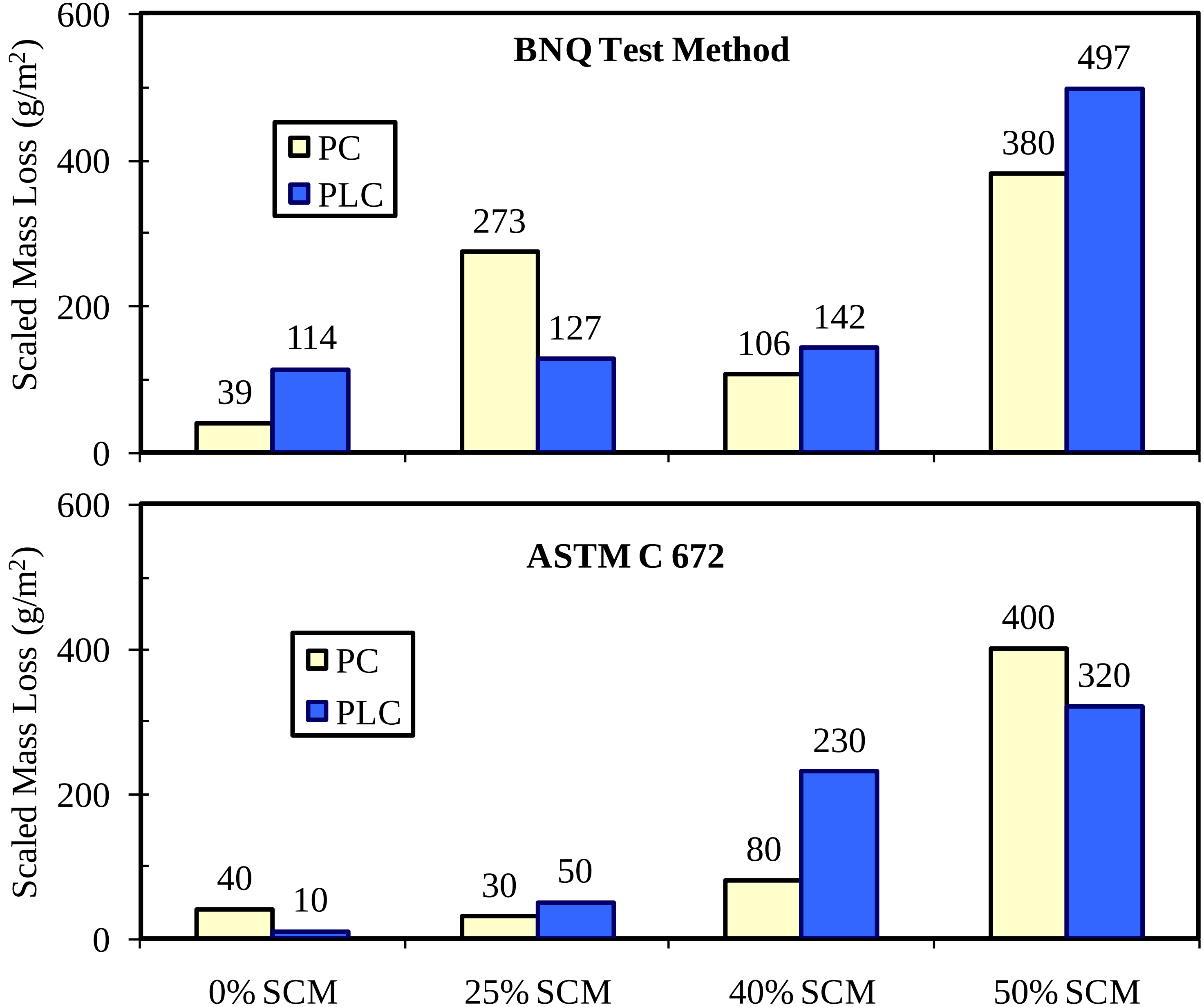
Chloride Diffusion Coefficients

Cement	Charge Passed in 6 Hours (Coulombs			
	0% SCM	25% SCM	40% SCM	50% SCM
PC	15.0	3.77	1.51	1.25
PLC	11.9	2.91	1.22	1.81

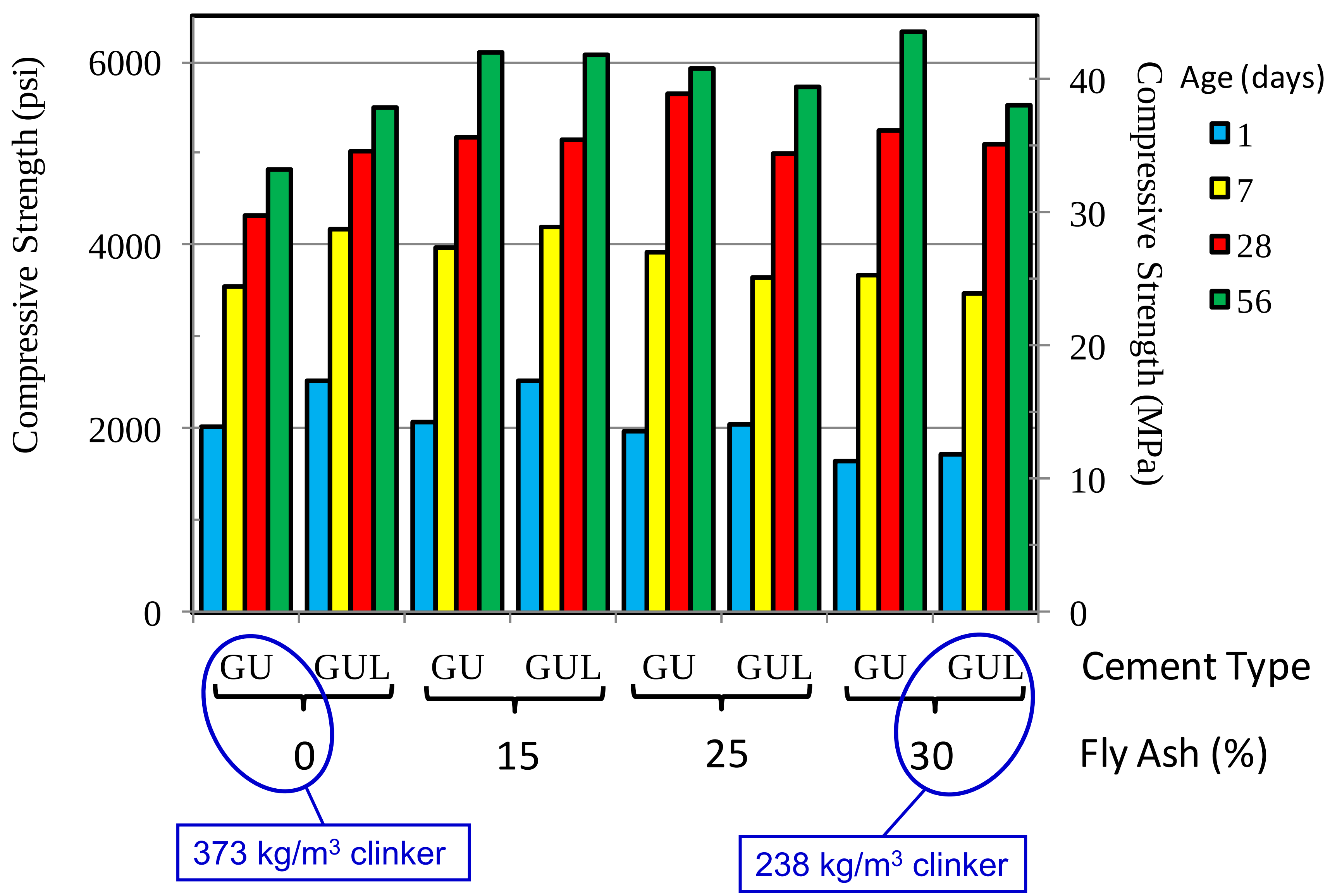


PLC Trial Pour at Gatineau - Chloride Profiles for Cores taken at 35 Days and Immersed in NaCl for 42 Days
Chloride (% by mass of concrete)
Depth (mm)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
PC - 0% SCM
PLC - 0% SCM
PC - 25% SCM
PLC - 25% SCM
PC - 50% SCM
PLC - 50% SCM

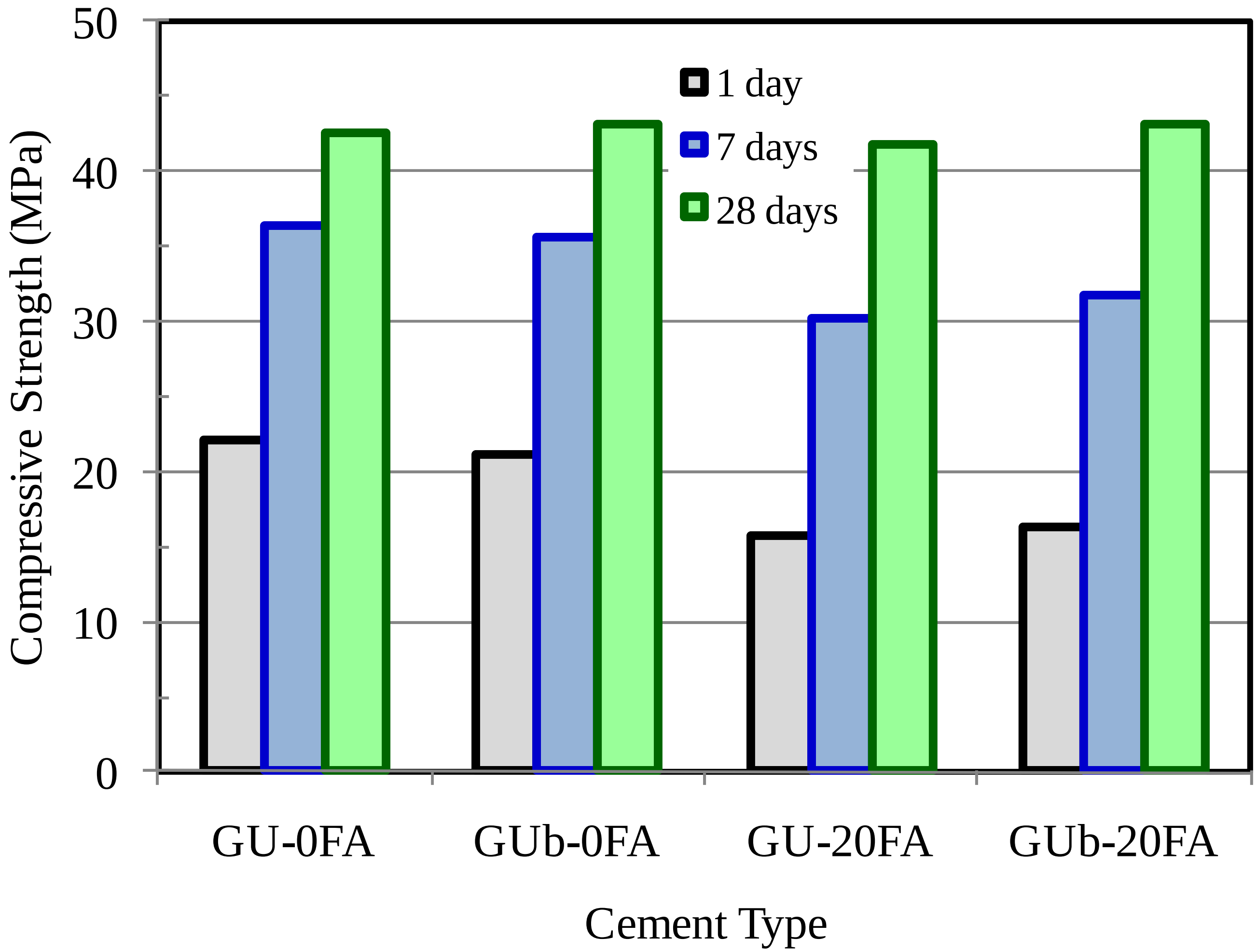
PLC Trial Pour at Gatineau – Scaling Test Results



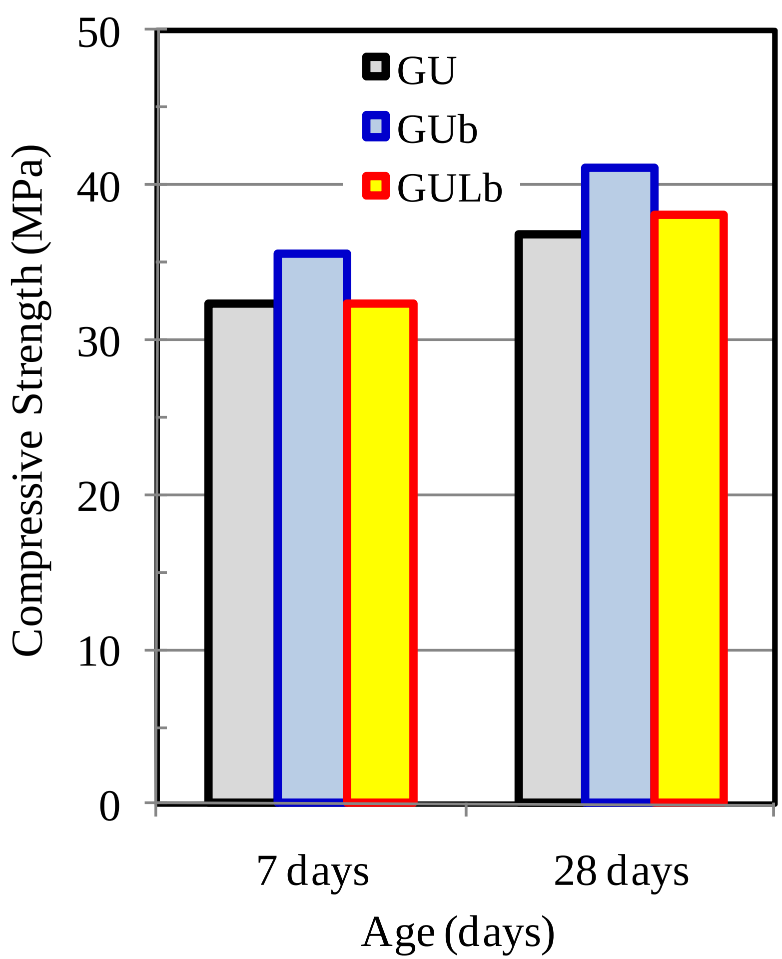
PLC Trial Pour at Exshaw – Cylinder Strengths

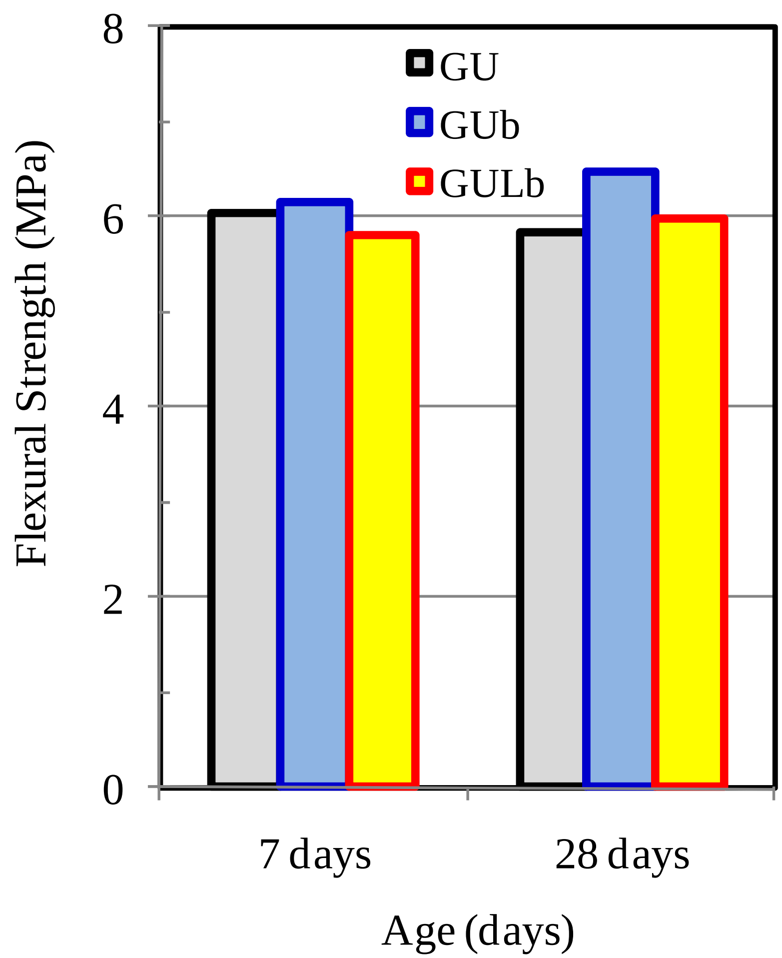


Initial Trials at Brookfield – Type GU versus Type GUb – with & without Fly Ash



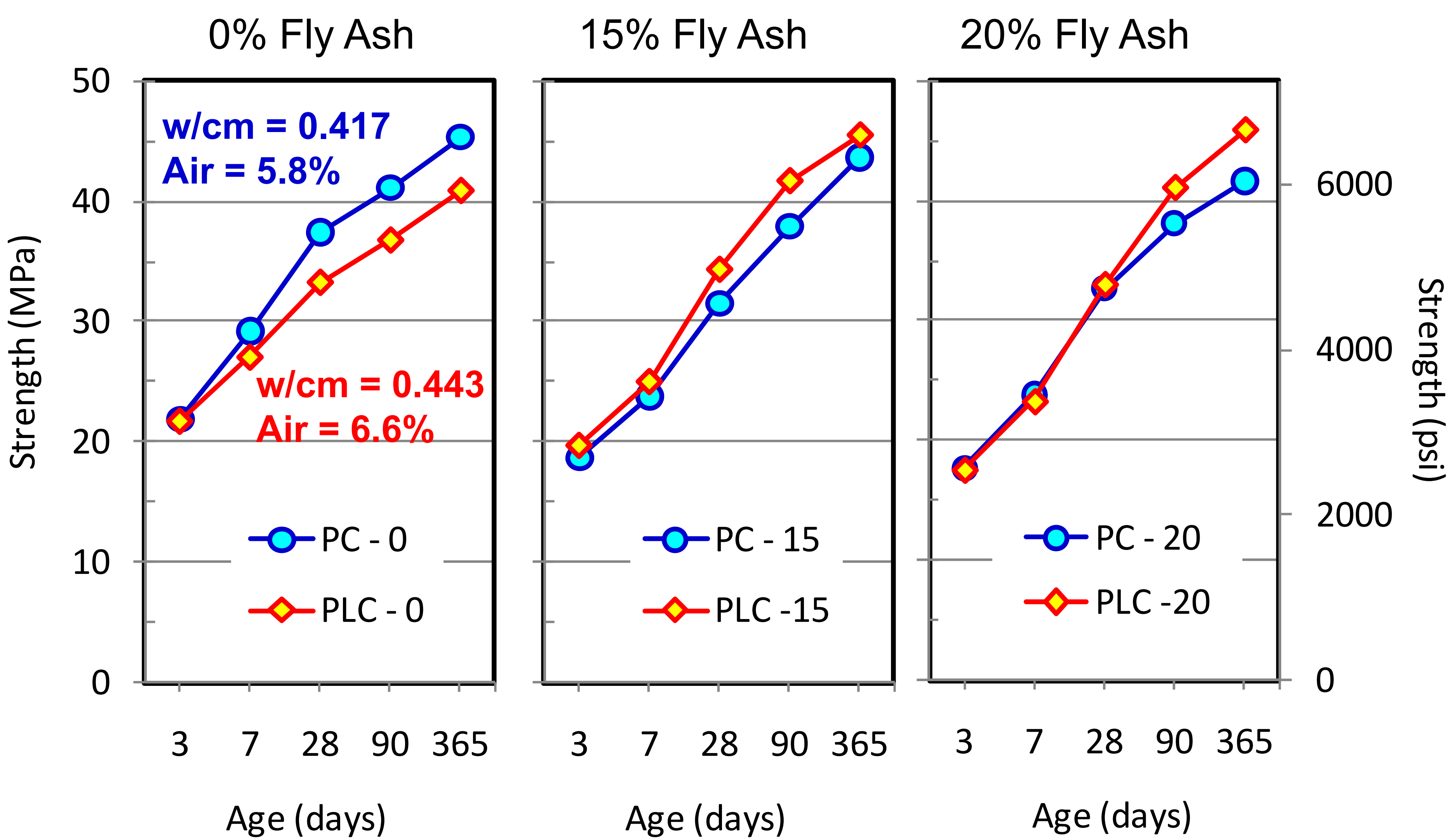
Laboratory Mixes at Brookfield – Type GU, Type GUb & Type GULb

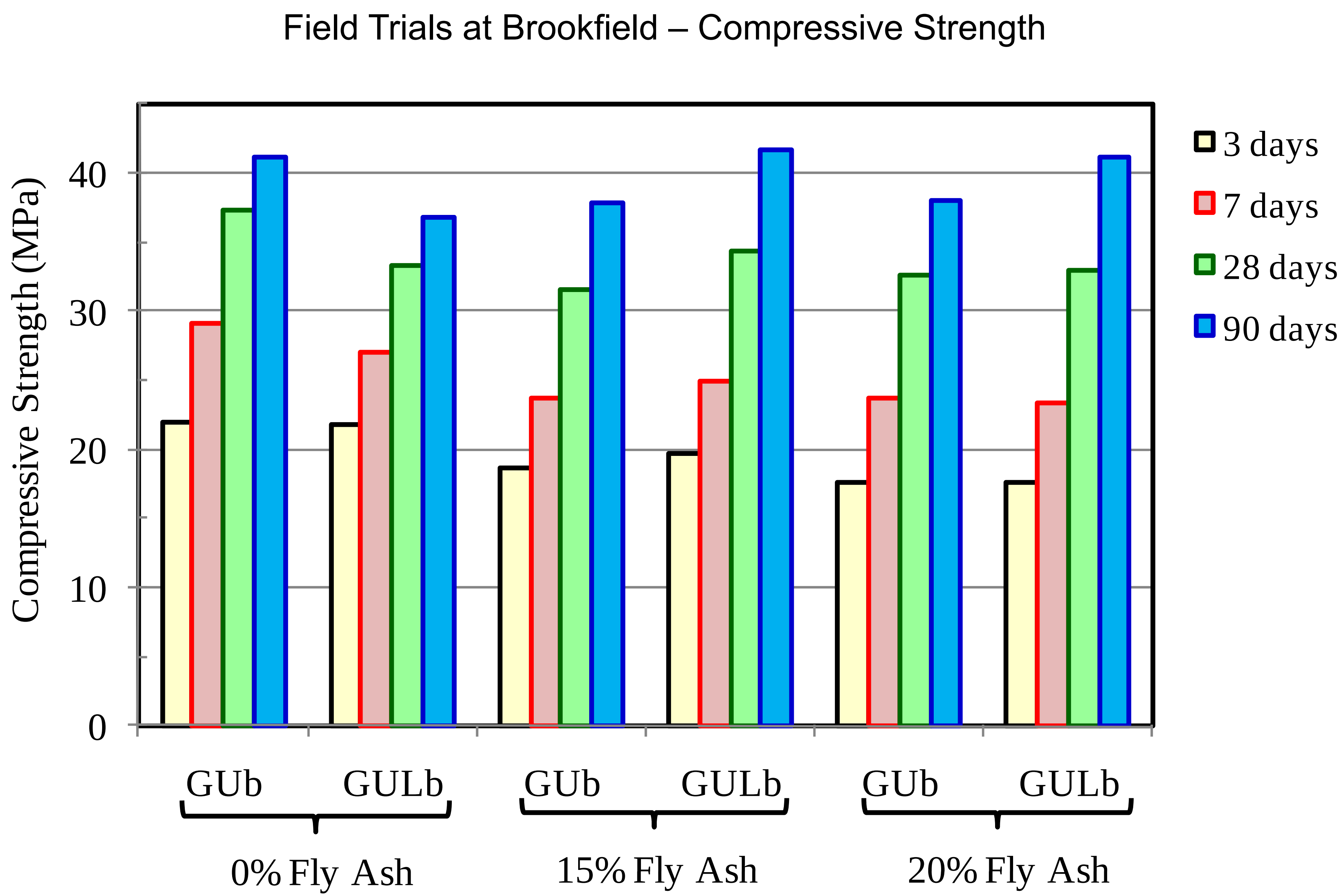


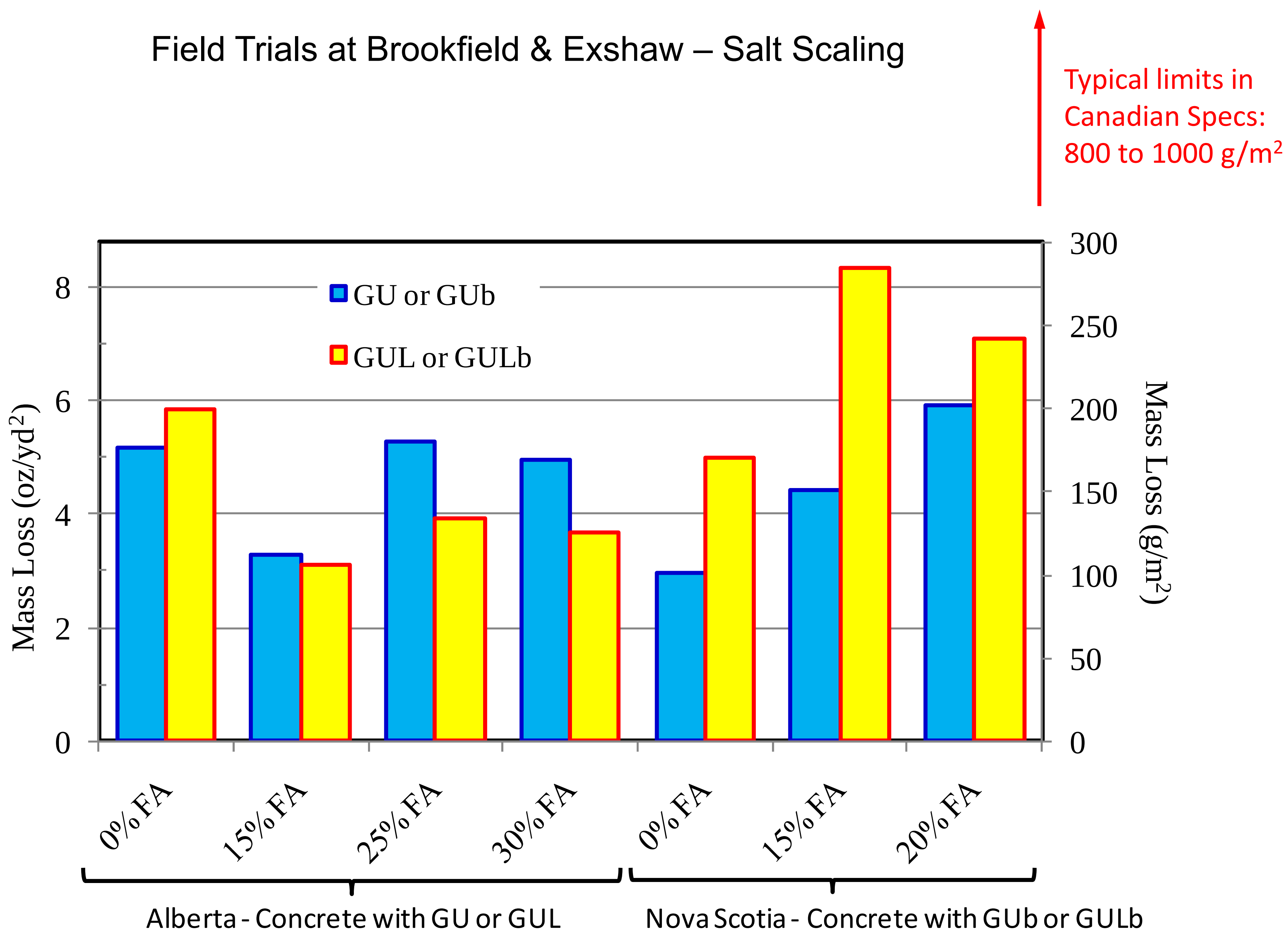


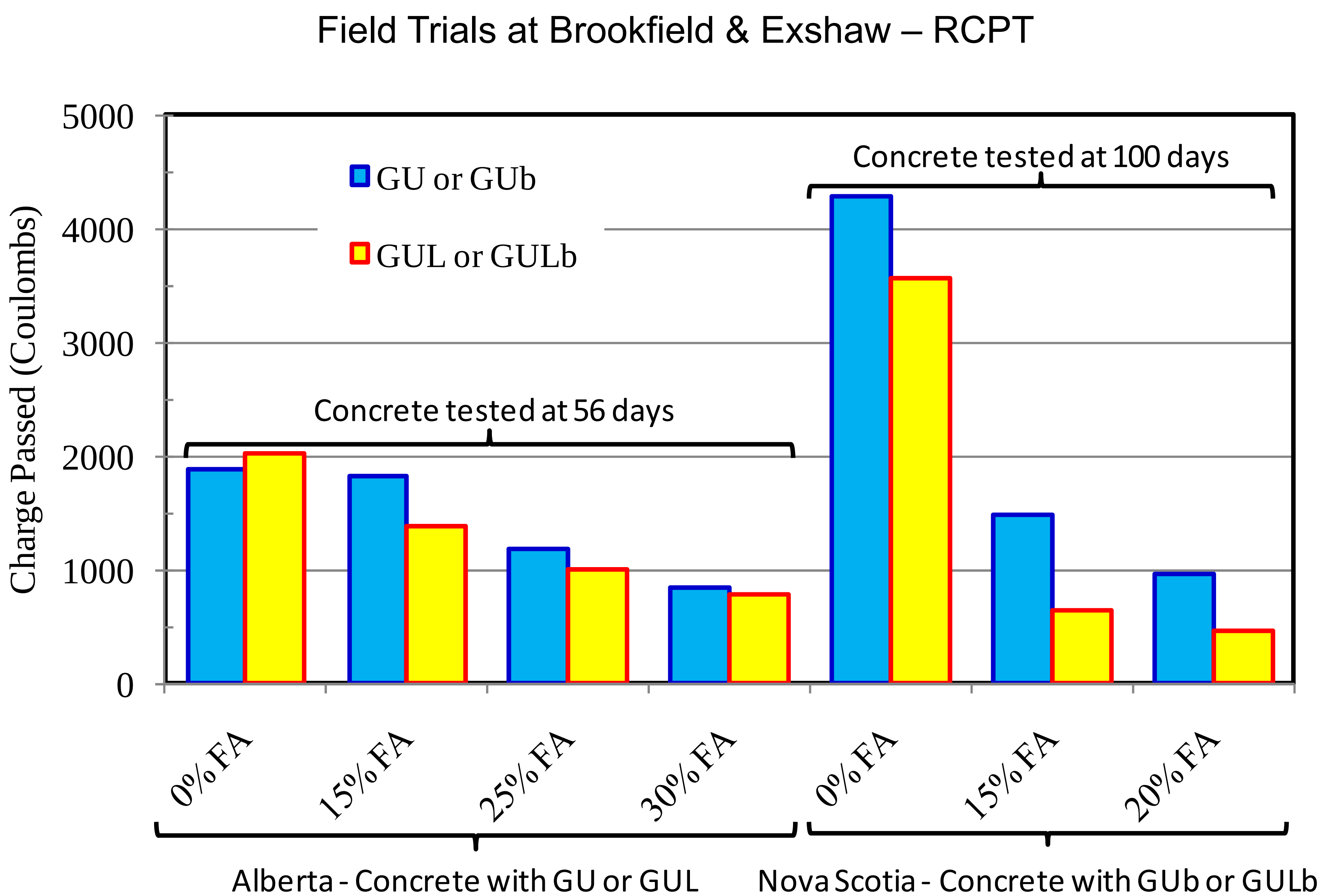
	Gypsum (%)	Limestone (%)	Slag (%)	**Clinker (%)**	Target Blaine (m^2/kg)
Type GU	5	4	0	**91**	380
Type GUb	5	0	15	**80**	450
Type GULb	5	12	15	**68**	500

Field Trials at Brookfield – Compressive Strength

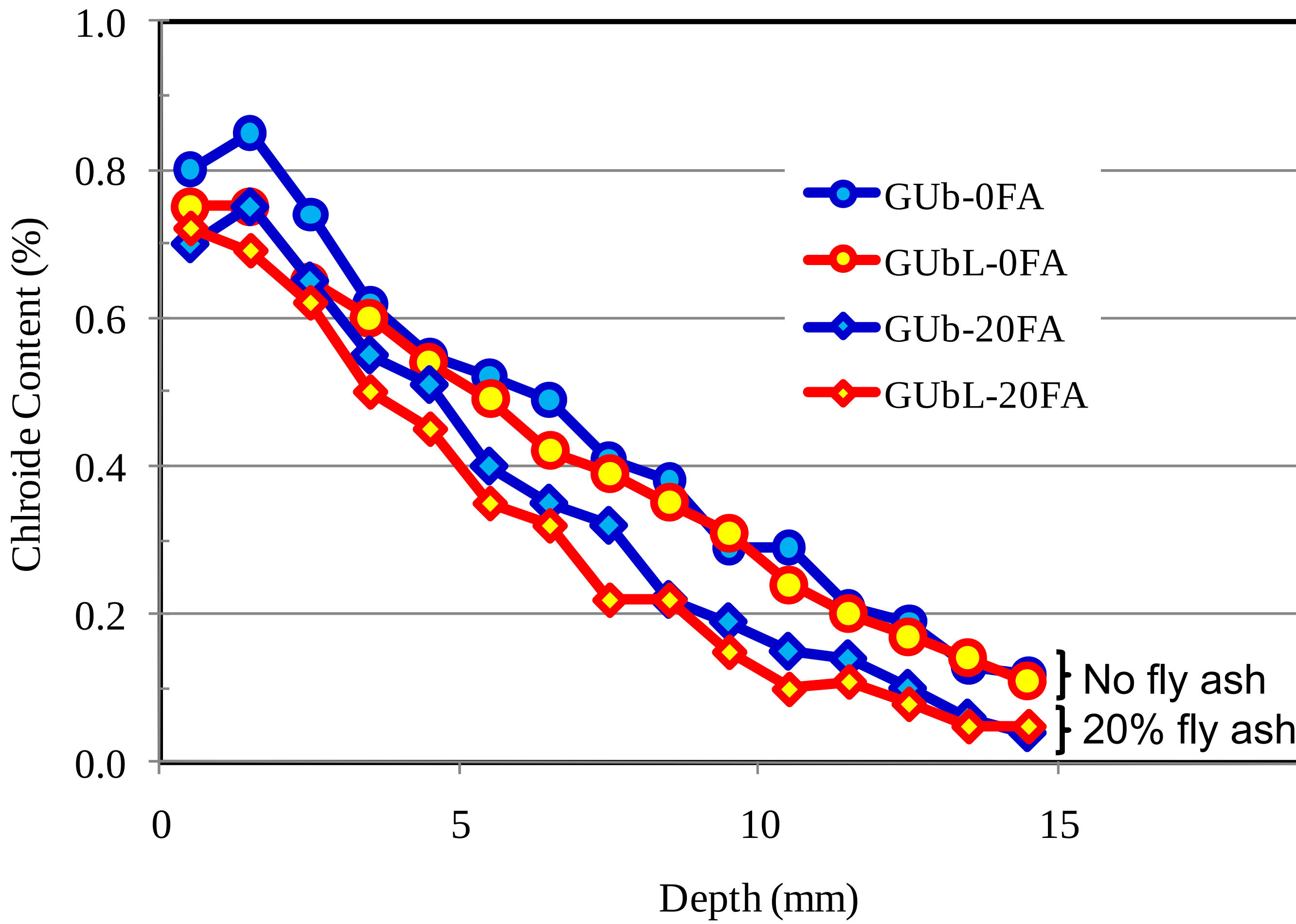



Field Trials at Brookfield – Compressive Strength
Compressive Strength (MPa)
0
10
20
30
40
3 days
7 days
28 days
90 days
GUb
GULb
GUb
GULb
GUb
GULb
0% Fly Ash
15% Fly Ash
20% Fly Ash


Field Trials at Brookfield & Exshaw – Salt Scaling
Typical limits in
Canadian Specs:
800 to 1000 g/m²
GU or GUb
GUL or GULb
Mass Loss (oz/yd²)
Mass Loss (g/m²)
0
2
4
6
8
0
50
100
150
200
250
300
0% FA
15% FA
25% FA
30% FA
0% FA
15% FA
20% FA
Alberta - Concrete with GU or GUL
Nova Scotia - Concrete with GUb or GULb


Field Trials at Brookfield & Exshaw – RCPT
Charge Passed (Coulombs)
5000
4000
3000
2000
1000
0
GU or GUb
GUL or GULb
Concrete tested at 56 days
Concrete tested at 100 days
0% FA
15% FA
25% FA
30% FA
0% FA
15% FA
20% FA
Alberta - Concrete with GU or GUL
Nova Scotia - Concrete with GUb or GULb

Field Trials at Brookfield – Chloride Diffusion Coefficients



$$C_x = C_0 \left(\frac{x}{\sqrt{4D_a \cdot t}} \right)$$

	No Fly Ash		20% Fly Ash	
	GUb	GULb	GUb	GULb
D_a (x 10^{-12} m^2/s)	6.1	6.4	3.9	3.4

Brookfield Cement Plant, Nova Scotia

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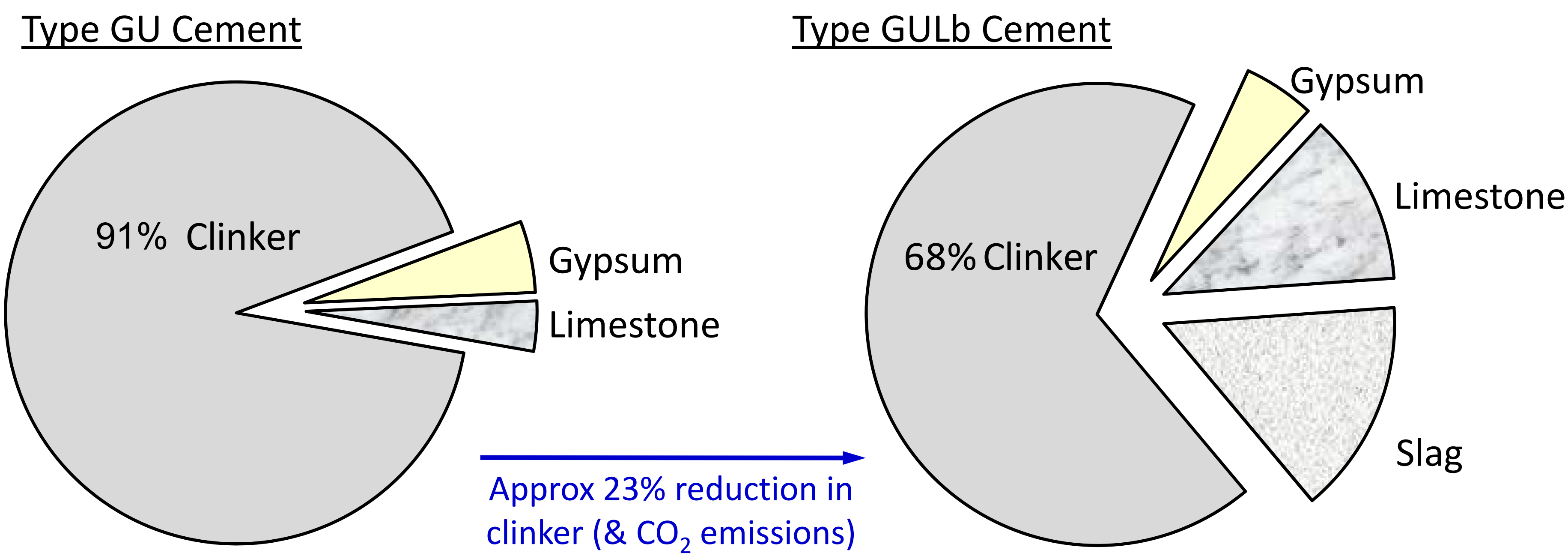
Type GU	5	4	0	91	380
Type GUb	5	0	15	80	450
Type GULb	5	12	15	68	500

- Type GULb contains 23% less clinker than Type GU

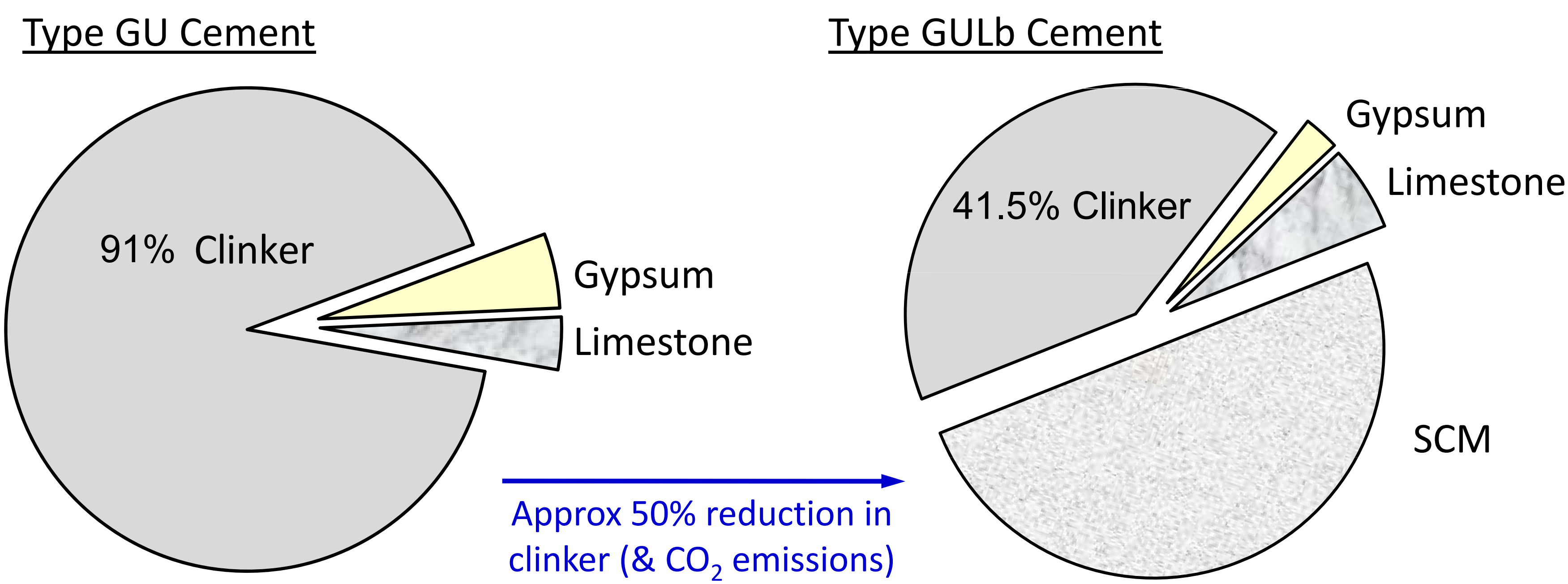


Further Clinker Reductions Made at Ready-Mixed Concrete Plant !!

Mixes used in Gatineau Field Trial

Concrete Mix	**Composition of Binder (%)**			
	Gypsum	Limestone	SCM	Clinker
GU + 0% SCM	5	4	0	91
GUL + 50% SCM	2.5	6	50	41.5

- Mix with GUL + 50% SCM contains approximately 50% less clinker in the binder than mix with straight Type GU cement



Gatineau Field Trial

Clinker Contents of Mixes used for Paving Trials (355 kg/m^3 cementitious material)

Concrete Mix	**Clinker in Cement (%)**	**Clinker in concrete without SCM (kg/m^3)**	**Clinker in concrete with 50% SCM(kg/m^3)**
GU + 0% SCM	91	**323**	162
GUL + 50% SCM	83	295	**147**

- 176 kg/m^3 reduction in cement clinker (= 176 kg/m^3 reduction in CO_2) by combined use of Type GUL cement plus SCM compared with Type GU
- **CO_2 reduced by almost 1½ tonne per 8-m^3 truck**

- 293 lb/yd^3 reduction in cement clinker (= 293 lb/yd^3 reduction in CO_2) by combined use of Type GUL cement plus SCM compared with Type GU
- **CO_2 reduced by almost 1 ton per 8-yd^3 truck**

Overall Summary

- Portland-limestone cement (PLC) with 12% limestone, when optimized for equal strength, can provide equivalent performance to Portland cement (Type PC)
- Blended portland-limestone cement with 12% limestone and 15% slag also provided equivalent performance to PC with 23% less clinker
- PLC performs well with (further) additions of SCM at the ready-mixed concrete plant (providing further opportunities to reduce CO_2 emissions).
- Using a combination of PLC or blended PLC together with (further) SCM additions at the concrete plant provides the opportunity to reduce the clinker content of paving mixes by up to 50%. Such reductions can translate to CO_2 reductions of the order of 1 to 1½ tons per concrete truck!