Lowering the Carbon Footprint of Concrete by Reducing the Clinker Content of Cement

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Abstract

In the past few decades significant efforts have been made to reduce the CO_2 emissions associated with the manufacture of portland cement mainly by making the process more energy efficient and increasing the use of alternative fuels. Further reductions in CO_2 can be achieved by lowering the clinker component of the cement as the pyroprocessing used to manufacture clinker produces approximately 1 tonne of CO_2 for every tonne of clinker. Traditionally reductions in the clinker content of cement have been achieved by producing blended cement consisting of portland cement combined with a supplementary cementing material (SCM). In Canada, it is now permitted to intergrind up to 15% limestone with cement clinker to produce Portland limestone cement or blended Portland limestone cement. Recent trials were conducted at the Brookfield cement plant in Nova Scotia to evaluate the performance of a blended cement containing 15% ground granulated blastfurnace slag (an SCM) with that of a blended Portland limestone cement containing the same amount of slag plus 12% interground limestone. The performance was evaluated by constructing a section of concrete pavement using a number of concrete mixes produced with the two cements plus various amounts of fly ash (another SCM) added at the ready-mixed concrete plant. A wide range of laboratory tests were performed on specimens cast on site during placing of the pavement. The results of these tests indicate that cements were of equivalent performance.

INTRODUCTION

An oft quoted statistic is that the production of every tonne of Portland cement (or clinker) releases an equivalent mass of CO_2 into the atmosphere. In actual fact, the amount of CO_2 released varies significantly depending on the energy efficiency of the plant and modern-day kilns with precalciner towers produce significantly less CO_2 per tonne of clinker than older kilns. Approximately half of the CO_2 emissions result from the burning of fossil fuels (coal, oil or gas) in the kiln to bring the raw feed to its clinkering temperature of 1450°C and, undoubtedly, future improvements in energy efficiency will provide for further reductions in CO_2 emissions. However, the other half of the CO_2 emissions results from the calcination of the limestone ($CaCO_3 \xrightarrow{heat} CaO + CO_2$) in the kiln, which is an inevitable part of the process of manufacturing Portland cement clinker that results in the production of approximately 0.5 tonnes of CO_2 for every tonne of clinker produced. This amount can be reduced to a certain degree by using non-carbonate sources of calcium (e.g. metallurgical slags), but limestone remains the predominant component of the raw feed in Portland cement kilns. After the clinker is produced in the kiln it is interground with various forms of calcium sulfate (principally gypsum) to produce the finished product, Portland cement. A typical "pure" Portland cement will contain about 95% clinker. Cement specifications in North America (ASTM, AASHTO, CSA) permit up to 5% limestone to be added to Portland cement and most Portland cements available today will have clinker contents in the range of 91 to 93% (the remainder being limestone and gypsum).

One measure for reducing the CO_2 footprint of Portland cement is to reduce the clinker content of the cement. Historically this has been achieved by producing blended cements consisting of portland cement combined with supplementary cementing materials (SCM) such as fly ash, slag, silica fume and natural pozzolans. Specifications for blended cements have been produced by ASTM, AASHTO and CSA, and such cements have been used in North America for decades. Another approach is to produce Portland limestone cements (PLC) which contain more than 5% limestone. PLC has been used in Europe for decades and current European specification (ENV 197) allows up to 20% limestone in CEM II/A cements and up to 35% in CEM II/B cements. In 2008, the Canadian specification for cement (CSA A3001-08) introduced a new classification of cement, this being Portland Limestone Cement (PLC) containing up to 15% limestone. Limestone can be used up to this level in all types of cement except for sulfate-resisting cements. The approach in Canada has been to intergrind the limestone with the Portland cement clinker and to optimize the grinding such that the PLC provides the same performance in concrete as does the equivalent type of Portland cement (PC). In other words, a concrete produced with Type GU (general use) Portland cement, which typically contains 3 to 4% limestone, will provide the same strength and durability as a concrete produced with Type GUL Portland limestone cement, which may contain up to 15% limestone. The equivalent performance provided by PC and PLC has been demonstrated in a number of studies (Hooton et al. 2010; Thomas, 2010a; 2010b).

The current version of the CSA A3001-08 does not permit blended Portland limestone cements. However, it was recently balloted to allow such cements containing between 5 to 15% limestone and one or more SCM. The limestone must be interground with the cement clinker whereas the SCM may be interground with the clinker and limestone or it may be blended with the finished PLC. Such cements will be designated GULb (for general use cement) as compared with the existing designation of GUb for blended cements produced with Portland cement.

This paper presents data from laboratory and field studies on the performance of concrete produced with blended Portland cement containing 15% slag and blended Portland limestone cement containing 15% slag and 12% limestone.

EXPERIMENTAL DETAILS

Two cements were produced at the Brookfield cement plant in Nova Scotia. The first was a blended Portland cement containing 3 to 4% limestone and 15% slag, and meets the requirements for Type GUb-15S cement in CSA A3001-08. The second cement was a blended Portland limestone cement containing 12% limestone and 15% slag; this cement meets the requirements for a Type GULb-15S cement, which will be included in the next amendment of CSA A3001. In both cases the cements were produced by intergrinding Portland cement clinker, gypsum, limestone and ground granulated blastfurnace slag. The chemical analysis of these materials is given in Table 1. Also shown is the analysis for the Type GU cement produced from the same clinker. Regarding the designations, Type GU, Type GUb-15S and Type GULb-15S, the "GU" refers to the fact that the cement is a general use cement, "b" indicates that the cement is a blended cement (contains SCM), the "L" indicates that the cement contains between 5% and 15% interground limestone, and 15S indicates that the blend contains 15% of a Type S (slag) SCM. Note that Type GU cements in Canada may contain up to 5% limestone, however, most Type GU cements will contain less than this amount (typically 3 to 4%) in order to meet the maximum LOI and/or insoluble residue limits for Type GU cement.

The other SCM used in this study is a Type F fly ash. The results of the chemical analysis performed on the fly ash are given in Table 1.

Initial trial mixes were conducted in the laboratory to compare the performance of the blended cement, Type GUb-15S, with the normal Portland cement, Type GU, produced at the plant.

In October 2009, six concrete mixtures were produced at a ready-mixed concrete plant in Truro, Nova Scotia, and were delivered to the Brookfield cement plant to construct a length of pavement just outside the main entrance to the plant (see Figure 1). The total volume of concrete placed was 232 cubic metres. Details of the six concrete mixtures are given in Table 2.

During placement of the concrete pavement, concrete specimens were cast on site for the following laboratory tests:

- Compressive strength, ASTM C 39
- "Rapid chloride permeability test" (RCPT), ASTM C 1202
- Deicer salt scaling test, ASTM C 672

Concrete specimens were cured under wet burlap and plastic in an unheated building for 24 hours and were transported to the laboratory where they were stripped and subjected to standard laboratory curing conditions.

Cores were taken from four of the sections, two with 0% fly ash and two with 20% fly ash, at an age of 2 months. These cores were stored in water at laboratory temperature for 28 days and then tested to determine the apparent chloride diffusion coefficient by bulk diffusion in accordance with test method ASTM C 1556. For this test, 50-mm lengths of core were sealed with epoxy on all but one flat face. The cores were then vacuum-saturated in limewater prior to immersion in a solution of sodium chloride (165 g/L) for 90 days. After 90 days the cores were placed in a milling machine and dust samples were ground from the surface in 1-mm increments down to a depth of 15 mm. The dust samples were analysed for chlorides to establish a concentration profile. Eqn. 1, a numerical solution of Fick's Second Law of Diffusion, was fitted to the experimental data using least squares to obtain the diffusion coefficient, D_a, and the surface concentration, C_0:

$$C_x = C_0\left(\frac{x}{\sqrt{4Dt}}\right) \qquad \text{Eqn. 1}$$

Where x is the depth (m), t is time (s), D_a is the apparent diffusion coefficient (m^2/s), C_x is the chloride concentration at depth x and time t, and C_0 is the chloride content at the surface (x = 0). Note that C_x and C_0 can be expressed in any units provided that they are the same units.

Flexural strength tests (ASTM C 78) were performed on beam samples produced from separate mixes produced in the laboratory. These mixes had a cement content of 360 kg/m^3, w/cm = 0.44 to 0.45, and contained no fly ash. In addition to casting mixes with the Type GUb and GULb cements, a third mix was cast with the normal Type GU Portland cement (3-4% limestone and no slag) produced at the Brookfield plant.

TEST RESULTS

Figure 2 shows the test results from the initial trial mixes comparing the Type GU and Type GU-15S cements produced at the same plant. The data show reductions in the strength of concrete, especially at early age, when 20% fly ash is used to partially replace the cement at the concrete mixer. However, for a given level of fly ash, there is no significant difference in the performance due to the cement type, indicating that 15% slag can be interground with the cement without jeopardizing performance. Type GUb has been produced at Brookfield and used by a number of producers in the Maritimes for a number of months and there is no indication of reduced performance on concrete produced with this cement compared with the regular Type GU from the same plant. It should be noted that the Type GUb is ground to a higher fineness (target Blaine 450 m^2/kg) compared with the Type GU (target 380 kg/m^2).

Figure 3 shows the strength results for concrete cast during the placement of the pavement. For concrete mixes with 15% and 20% fly ash there was no consistent significant difference between the strength of mixes cast with Type GUb versus GULb, except that GULb mixes had slightly higher 90-day strengths. For the mixes without fly ash, the strengths were similar at 3 days, but the mix with Type GULb showed lower strengths (by about 10%) at the later ages. It should be noted that the mix with GULb had a slightly higher w/cm (by 0.02) and significantly higher air content (by 0.8%) compared to the mix with GUb and this could partially explain this discrepancy (note a 1% increase in air can reduce the strength by approximately 5.5%).

Figure 4 shows the results of RCPT tests conducted on concrete samples at an age of 90 days. The partial replacement of either cement with fly ash has a profound effect on the charge passed in this test. Mixes without fly ash are classed as concrete with high chloride penetrability by the criteria in ASTM C 1202, mixes with 15% fly ash are classed as low to intermediate penetrability, and mixes with 20% fly ash are classed as low penetrability. Comparing mixes with the same fly ash content, those produced with Type GULb showed lower chloride ion penetrability compared with mixes with Type GUb; the differences are considered to be significant.

Results from deicer scaling tests are shown in Figure 5. There is no consistent difference with fly ash content. At each level of fly ash the scaled mass loss is slightly higher for the Type GULb cement compared with the Type GUb cement. However, differences are small and in all cases the scaled mass loss can be considered very low and well below typical limits used in Canada (e.g. maximum allowable losses from 800 to 1000 g/m^2).

Figure 6 shows chloride concentration profiles for concrete after soaking specimens in 165 g/L NaCl solution for 90 days. Calculated diffusion coefficients are presented in Table 4. It is clear that partially replacing 20% of the cement with fly ash increases the resistance of the concrete to chloride ion penetration. However, there is no consistent difference between the chloride resistance of concrete produced with either Type GUb or Type GULb cement.

Figure 7 shows compressive and flexural strength results for concretes produced in the laboratory with Type GU, GUb and GULb cements without fly ash. These data indicate very little significant difference between the strength of concrete produced with the three different cements.

DISCUSSION

Research in Canada (Hooton et al. 2010; Thomas, 2010a; 2010b) has shown that it is possible to produce Portland limestone cement (PLC) with up to 15% interground limestone that will provide the same performance characteristics as Portland cement (PC) provided the grinding of the PLC is optimized. This is generally achieved by grinding the PLC to have a fineness approximately 100 to 120 m^2/kg (Blaine) greater than PC (Thomas et al. 2010b). The increased fineness can be readily achieved because the limestone is softer than cement clinker and will be ground finer than the clinker when the products are interground. The very fine limestone particles act as nucleation sites for cement hydration products thereby increasing the rate of cement hydration (Soroka and Setter, 1977; Bonavetti et al, 2003) and this often leads to higher early age strengths.

In this paper it has been demonstrated that a blended PLC with 15% slag and 12% limestone (Type GULb) can be produced to provide equivalent performance as a blended cement containing Portland cement and 15% slag (Type GUb). Both these cements gave similar performance to normal Portland cement (Type GU) produced from the same clinker. To achieve similar performance with these three cements, plant trials have indicated that the target Blaine increases as follows: Type GU – 380 m^2/kg, Type GUb – 450 m^2/kg, Type GULb – 500 m^2/kg.

The Type GULb cement contains approximately 23% less clinker than the Type GU cement from Brookfield cement and this represents a very significant reduction in the CO_2 associated with the finished cement. Given that the cements can be produced to provide equivalent performance in concrete it is possible that Type GU cement could eventually be replaced by Type GULb cement. Given that the Brookfield plant produces approximately 300,000 tonnes of cement annually, switching to Type GULb cement could reduce the CO_2 emitted from the plant by approximately 70,000 tonnes each year.

Type GULb cement would be suitable for use in virtually all concrete mixes produced at most ready-mixed concrete plants, the exception being concrete mixes that will be used in sulfate exposure classes. The ready-mixed producer then has an option to further reduce the CO_2 footprint of the concrete by partially replacing the cement with fly ash and slag. For example, consider the mix containing Type GULb and 20% fly ash used to construct some of the paving sections in the current study. This mix contains approximately 140 kg/m^3 less cement clinker than would a similar mix produced with straight Type GU cement from the same plant. This translates to a similar reduction in the CO_2 emitted for each cubic metre of concrete. In other words, one 7-m^3 truck leaving the ready-mixed concrete plant would have about 1 tonne less CO_2 associated with the concrete if that concrete was produced using a blend of Type GULb cement and 20% fly ash compared with a similar truck containing an equivalent mix produced with Type GU cement alone. Of course, in many applications it is possible to increase the amount of cement replaced by fly ash to more than 20%. In a previous field trial in Quebec (Thomas et al. 2010a) up to 50% of PLC was replaced by a blended SCM consisting of 2 parts slag and 1 part fly ash. In this mix the clinker only constituted approximately 41 to 42% of the total mass of cementing materials compared with about 91 to 92% clinker for an equivalent mix produced with straight PC.

The combined use of blended PLC (Type GULb) and mixer-added SCM can result in very substantial reductions in the CO_2 footprint of concrete. It is possible that alumina present in SCM such as fly ash and slag increases the potential for the formation of carboaluminates, but this phenomenon needs to be confirmed by further research.

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Table 1 Chemical Analysis of Cementitious Materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O_e	SO_3	LOI	%-pass 45 µm	Blaine (m^2/kg)
GU	21.1	5.1	2.2	63.6	2.0	0.83	3.8	1.9	94.5	365
GUb-15S	22.9	5.9	1.9	59.3	3.2	0.89	4.1	0.6	98.6	453
GULb-15S	22.4	5.7	1.8	57.1	3.4	0.85	4.0	6.15	97.1	532
Fly Ash	48.0	20.7	7.92	6.68	-	1.48*	3.08	1.43	90.4	-

*Available (equivalent) alkalis

Table 2 Details of Initial Trial Mixes Comparing Type GU and Type GUb Cements

	No Fly Ash		20% Fly Ash	
	GU-0FA	GUb-0FA	GU-20FA	GUb-20FA
Type GU (kg/m^3)	355	-	284	-
Type GUb (kg/m^3)	-	355	-	284
Fly Ash (kg/m^3)	0	0	71	71
W/CM	0.54	0.54	0.51	0.51
Air Content (%)	1.4	1.5	6.1	6.2
Slump (mm)	110	100	95	100

Table 3 Details of Concrete Mixtures used for Pavement Construction and Laboratory Tests

	No Fly Ash		15% Fly Ash		20% Fly Ash	
	GUb-0FA	GULb-0FA	GUb-15FA	GULb-15FA	GUb-20FA	GULb-20FA
Type GUb (kg/m^3)	392	-	327	-	308	-
Type GULb (kg/m^3)	-	384	-	327	-	309
Fly Ash (kg/m^3)	0	0	57	58	77	77
Water (kg/m^3)	163	170	166	165	168	165
W/CM	0.42	0.44	0.43	0.43	0.44	0.43
AEA[1] (mL/m^3)	193	298	228	299	240	303
Retarder (mL/m^3)	175	175	188	181	171	181
WRA[2] (mL/m^3)	788	781	794	781	800	788
Air Content (%)	5.8	6.6	6.1	6.2	6.6	6.5
Slump (mm)	75	60	80	65	65	75

[1]AEA = air-entraining admixture

[2]WRA = normal-range water-reducing admixture

Table 4 Calculated Diffusion Coefficients from Bulk Diffusion Test (ASTM C 1556)

	No Fly Ash		20% Fly Ash	
	GUb-0FA	GULb-0FA	GUb-20FA	GULb-20FA
D_a (x 10^{-12} m^2/s)	6.1	6.4	3.9	3.4

Figure 1 Construction of Pavement at Brookfield Cement Plant – 3 October 2009

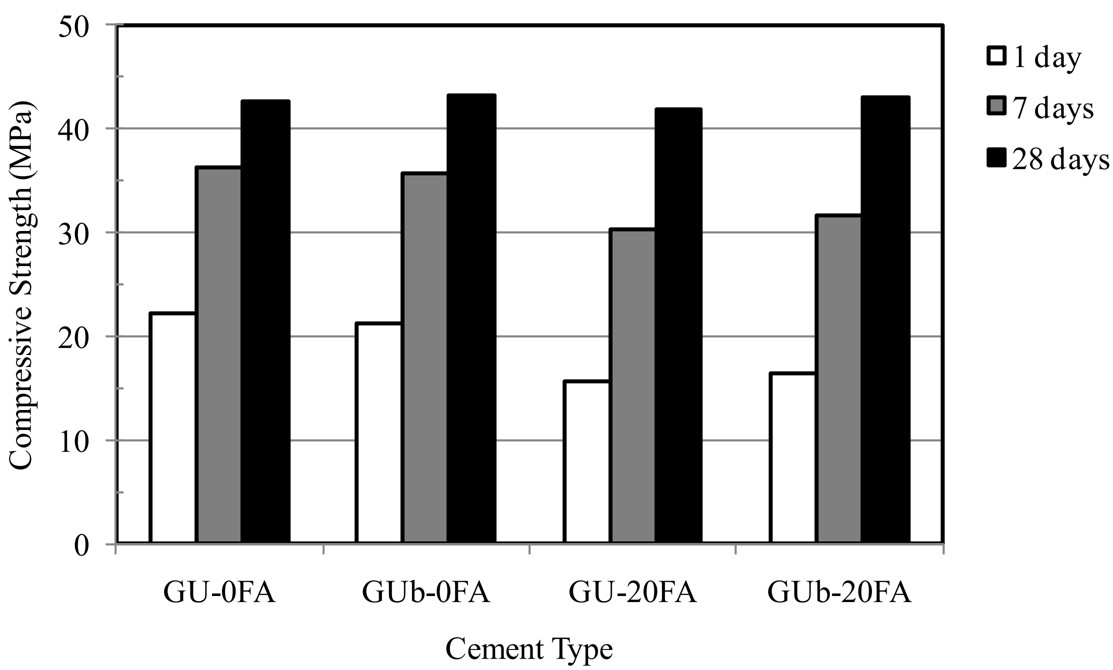

Figure 2 Strength Results for Initial Laboratory Trial Mixes Comparing Types GU and GUb-15S Cements

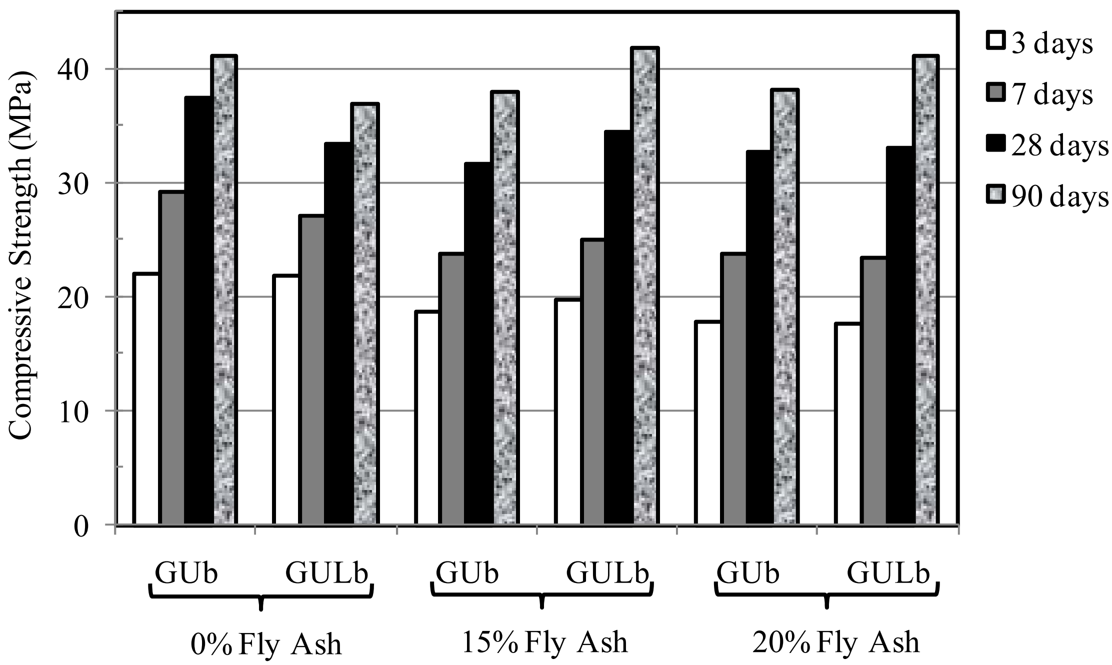

Figure 3 Strength Results for Concrete Cylinders Cast during Field Trial

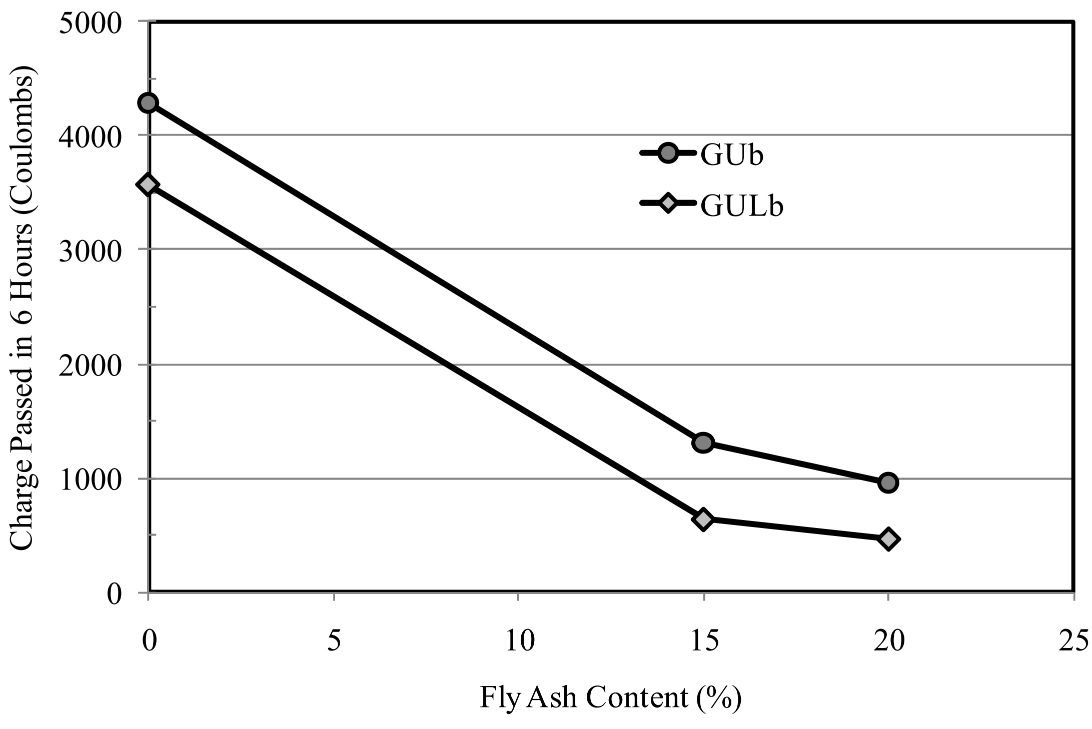

Figure 4 Results of Rapid Chloride Permeability Tests Conducted on 90-Day-Old Samples

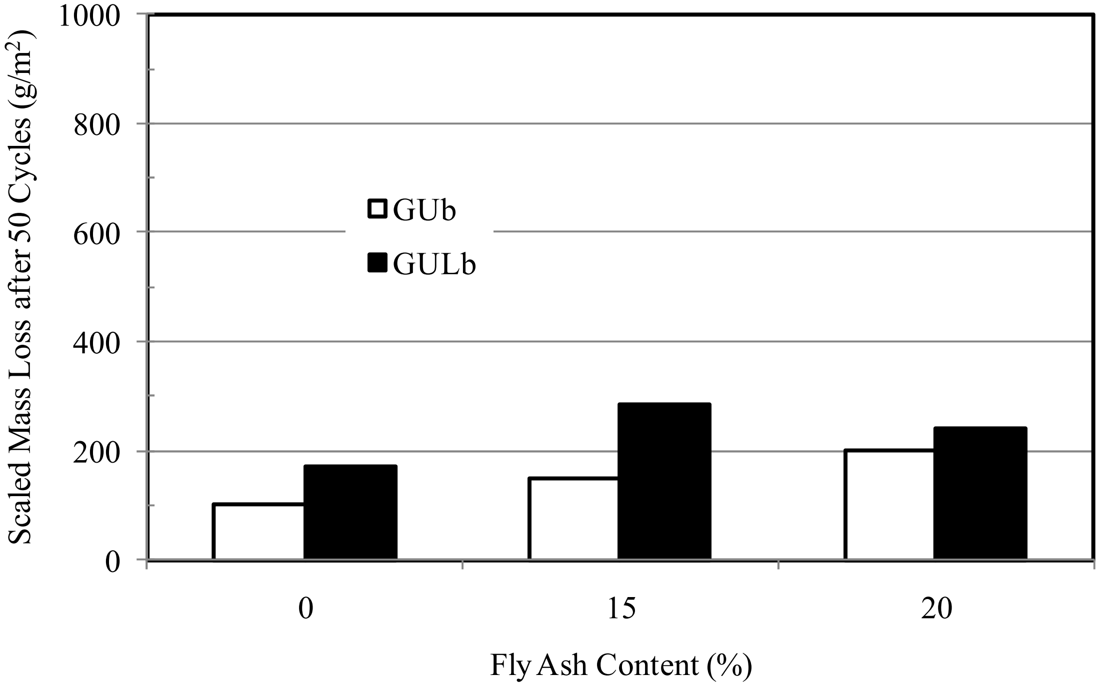

Figure 5 Results of Deicer Salt Scaling Tests

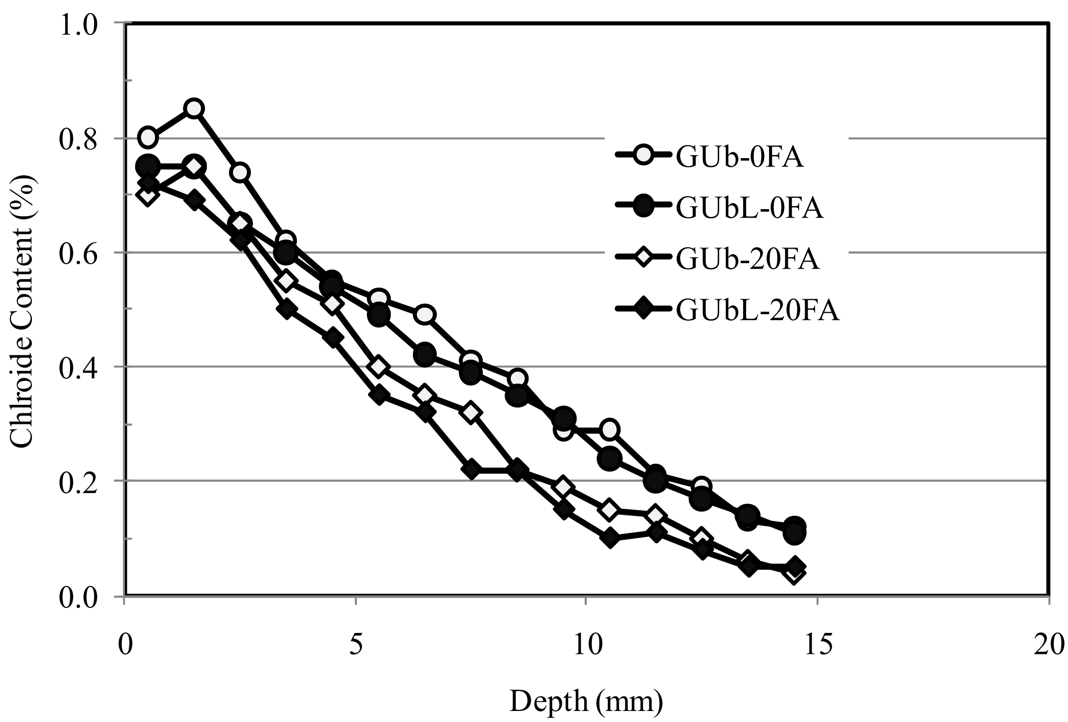

Figure 6 Chloride Profiles after 90 days Ponding in NaCl Solution

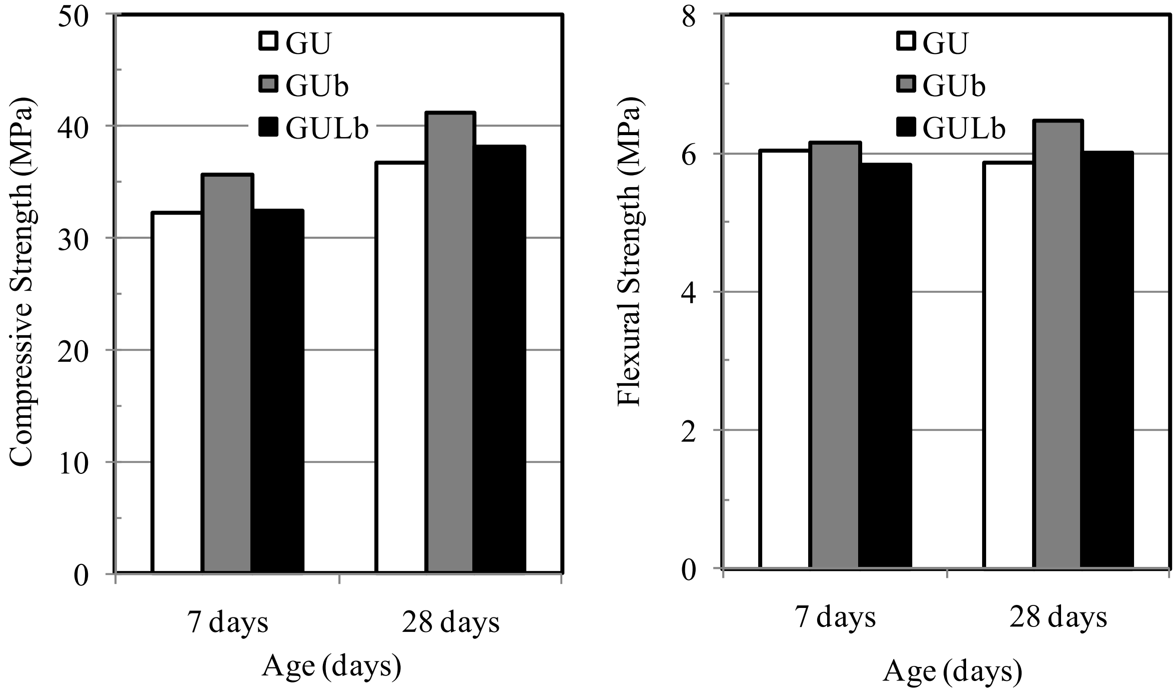

Figure 7 Strength Data for Concretes Produced with Type GU (4% limestone), Type GUb (4% limestone and 15% slag) and Type GULb (12% limestone and 15% slag) Cements