Maximizing carbon uptake and performance gain in slag-containing concretes through early carbonation

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ABSTRACT

Carbon dioxide (CO_2) emissions have been identified as a major contributor to climate change. Current CO_2 mitigation efforts focus on the removal, recovery and disposal of CO_2 at point sources. Finding beneficial uses of as-captured or recovered CO_2 is a critical challenge in greenhouse gas mitigation. This thesis investigates the possibility of the beneficial use of carbon dioxide in precast concrete production and the performance, both short-term and long-term, of the concretes so produced.

The calcium compounds in cementitious materials react readily with carbon dioxide to convert CO_2 to thermodynamically stable carbonates. The reaction accelerates strength development and makes the technology appropriate for early age curing. Paste, mortar and concrete samples were examined to quantify such aspects as the carbon dioxide uptake, strength development, and durability of carbonated concrete.

It was found that the uptake by the cementitious binders was significant. Compared to their theoretical capacity, cement could reach a carbonation degree of over 25% when treated as pastes and about 20% when used as a part of concrete. The study compared carbonation-cured and hydrated Portland cement concrete and slag cement concretes in terms of their early strength, late strength, weathering carbonation shrinkage, freeze/thaw durability, water absorption, and pH. The carbonated concrete was generally comparable, or superior, to the hydrated concrete except for the case of a 50% GGBF slag blend which had a slower strength development due to reduced secondary cementitious reaction.

A second method of binding carbon into concrete was considered by carbonating ladle slag fines and using them as a fine aggregate. The 28-day strength of concrete, either hydrated or carbonation-cured, made with the manufactured slag aggregate was comparable to that of a

hydrated concrete made with conventional fine aggregate. Carbon dioxide uptake by concrete was nearly doubled if carbonation-cured concrete employed carbonated ladle slag as a fine aggregate.

It is estimated that close to two million tonnes of CO_2 could be sequestered into precast concrete annually in US and Canada if four building products, namely blocks, pavers, cement boards and fibreboards, are processed using carbonation-curing. The approximately 110 million tonnes of cement produced in North America annually are associated with emissions of about 74 million tonnes of CO_2. The sequestration from carbonation-curing would represent an emission reduction of 2.7%. The capacity for carbon storage into precast concretes can be further increased if carbonation-treated aggregates are used.

SOMMAIRE

Les émissions de dioxyde de carbone (CO_2) contribuent de façon importante aux changements climatiques. Les efforts actuels de mitigation du CO_2 se concentrent principalement sur la saisie, la récupération et le débarras du CO_2 aux sources ponctuelles. Trouver des usages bénéfiques au CO_2 tel que la capturé ou récupération représente un défi critique pour la mitigation des gaz à effet de serre. Cette thèse examine la possibilité d'utiliser le CO_2 de façon bénéfique dans la production du béton préfabriqué, ainsi que la performance à court et à long termes du béton ainsi produit.

Les composés calcaires dans le ciment réagissent avec le dioxyde de carbone pour convertir le CO_2 en carbonates qui sont stables du point de vue thermodynamique. Cette réaction accélère le développement de la résistance du béton, ce qui rend la technologie appropriée pour des bétons à cure rapide. Des échantillons de pâte, de mortier et de béton ont été examinés pour tenter de quantifier certains aspects tels l'absorption du dioxyde de carbone, le développement de la résistance et la durabilité du béton carbonaté.

L'absorption du CO_2 par les liants dans le ciment fut importante. Comparé à leur capacité théorique, le ciment pourrait atteindre un degré de carbonation de plus de 25% quand il est préparé sous forme de pâte et de 20% quand il est utilisé dans le béton. L'étude a considéré des bétons composés de ciment Portland et de ciment de scories, curés de façon traditionnelle (hydratation) et curés par carbonatation, et a comparé leurs résistance après 7 jours, résistance après 56 jours, résistance à la contraction lors de la carbonatation, durabilité aux cycles de gel/dégel, absorption d'eau et pH. Le béton carbonaté était généralement comparable, ou

supérieur, au béton hydraté, sauf pour le mélange scories 50% GGBF, qui développe plus lentement sa résistance due à une réduction de réaction secondaire de ciment.

Une deuxième façon d'absorber le dioxyde de carbone dans le béton a été considérée en carbonatant des fines particles de laitier poche et en les utilisant comme granulats fins. La résistance du béton après 28 jours, soit hydraté ou carbonaté, fait avec les granulats scories manufacturés était comparable à celle du béton hydraté fait à partir de granulat fin conventionnel. L'absorption de dioxyde de carbone dans le béton était presque doublée si le béton curé par carbonatation employait du laitier poche carbonaté comme granulat fin.

Il est estimé que près de 2 millions de tonnes de CO_2 pourraient être séquestrées dans le béton préfabriqué annuellement, aux États-Unis et au Canada, si 4 produits de construction, notamment les blocs, les dalles, les panneaux (« cement boards ») et les panneaux de fibres agglomérés (« fibreboards »), étaient produits en utilisant la cure par carbonatation. La production de ciment en Amérique du Nord, qui atteint environ 110 millions de tonnes annuellement, est associée à des émissions d'environ 74 millions de tonnes de CO_2. La séquestration du CO_2 dans le processus de cure par carbonatation représenterait une réduction de 2,7% des émissions. La capacité de stockage du carbone dans le béton préfabriqué peut être augmentée davantage si des granulats traités par carbonatation sont utilisés.

ACKNOWLEDGEMENTS

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CONTRIBUTIONS OF AUTHORS

The manuscripts included in this thesis and Chapters 3 to 6 have been submitted for publication in scientific journals. The author was responsible for conducting the research, analyzing the data and preparing the manuscripts. The author's supervisor, Dr. Yixin Shao, provided general guidance and editorial revisions throughout the entire process. Dr. Caijun Shi was invited to review the work in Chapter 4 and similarly provided guidance and revisions.

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INTRODUCTION

OVERVIEW

Throughout history, Mankind has changed the world in which he lives for his own benefit. However, in many instances, his actions have resulted in many instances of unintended consequences. Presently, the world is dealing with the spectre of profound global climate change. Increasing environmental awareness has resulted in international agreements that recognize the contribution of anthropogenic greenhouse gas emissions to climate change. The challenge of mitigating these emissions is being met with action and research.

The Greenhouse Gas Effect and Climate Change

Life on Earth owes itself to the greenhouse effect, a natural process by which the atmosphere traps some of the Sun's energy and warms the Earth. When energy from the Sun reaches the planet, some 25% of it is reflected by the atmosphere back into space, 23% is absorbed by the atmosphere, 46% is absorbed by the land and oceans while 6% is reflected from the Earth's surface (National Weather Service 2007). The Sun's radiation that is absorbed on the Earth's surface will become heat energy in the form of long-wave infrared radiation. Some of this energy will return to space but certain atmospheric gases, called greenhouse gases or GHG, absorb infrared radiant heat. The warmed gas molecules are excited and will, in turn, emit infrared energy in all directions. Again, some of the energy emitted by the gas molecules is lost to space but some returns to warm the Earth's surface. Without the natural greenhouse effect, the Earth would have a chilly average temperature of about -19 °C rather than the presently hospitable 15 °C.

With the onset of the industrial revolution, human activity has greatly increased the atmospheric concentrations of greenhouse gases. Since that time, the climate system has unequivocally warmed, as evidenced from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global average sea level. The United Nations Intergovernmental Panel on Climate Change concluded in 2007 (IPCC 2007b) that “most of the observed increase in globally averaged temperatures since the mid-20th century is very likely due to the observed increase in anthropogenic greenhouse gas concentrations.”

Greenhouse Gases Emissions

The major greenhouse gases, summarised in Table 1.1, are carbon dioxide (emitted from the combustion of fossil fuels and deforestation), methane (released from rice paddies, landfill sites and livestock), N_2O (related to fertilizer use and automobile exhaust), and fluorinated compounds (used as refrigerants and propellants). While their concentrations may be modest, their influence is determined by their atmospheric lifetime (defined as the mean time that a molecule resides in the atmosphere before it is removed by chemical reaction or deposition) and radiative efficiency (a measure of the impact a gas has on the energy balance of the Earth-atmosphere system). The global warming potential of a greenhouse gas is determined by the atmospheric lifetime and radiative efficiency of the gas.

In terms of the proportions of the anthropogenic GHG emissions, carbon dioxide is the most important greenhouse gas. CO_2 emissions totalled 76.7% of the global anthropogenic greenhouse gas emissions in 2004 (Figure 1.1), with CO_2 resulting from the use of fossil fuels being 56.6%, while CO_2 from non-fossil fuel sources amounted to 20.1% of the total emissions. The non-CO_2 emissions, less than 24%, comprised the other major greenhouse gases, CH_4, N_2O, and fluorinated compounds.

Greenhouse gas emissions can be categorized by source. Emissions from residential, transportation and agriculture are widely distributed but of low intensity. Emissions that are related to energy production and industrial sources are high intensity point sources. These latter two sectors are the two largest contributors to greenhouse gas emissions with a 25.9% and 19.4% share of the total respectively (Figure 1.2).

Of the industrial emissions, the point source emissions can be attributed to a variety of specific processes. As shown in Table 1.2, the power generation sector, from sources such as coal-fired power plants, is responsible for the largest fraction of point-source CO_2 emissions.

The second most significant source of industrial CO_2 emissions is cement production. The production of clinker emits CO_2 that results from both the calcination of the raw materials and the burning of fossil fuels to meet the energy requirements. Currently, the specific emissions are about 670 kg of CO_2 emitted per tonne of clinker produced (World Business Council for Sustainable Development 2008) (the cement production emissions reported in Table 1.2 take into account the emissions associated with calcination but exclude those associated with the energy requirements). While efforts are being made to reduce the energy requirements of clinker production, one major producer believes that it would be difficult, owing to the inherent process of calcination, to reduce the total CO_2 emission below 610 kg per tonne of cement (Rosenthal 2007). Further, while the specific emissions per tonne of cement may decline, global cement production is projected to increase significantly to meet the increasing demands of developing countries and overall emissions will continue to be a concern.

Governmental Action on Climate Change

Global action on climate started at the United Nations Conference on Environment and Development (UNCED), held in Rio de Janeiro from June 3 to June 14, 1992. The event, commonly known as the Earth Summit, produced an international treaty called The United Nations Framework Convention on Climate Change (UNFCCC). The agreement had the stated objective of achieving "stabilization of greenhouse gas concentrations in the atmosphere at a level that would prevent dangerous anthropogenic interference with the climate system" (United Nations 1992). On June 12, 1992, 154 nations signed the UNFCCC, and the agreement entered into force on March 21, 1994 once the governments of 50 signatories had ratified the agreement.

Once the agreement entered into force, the parties have held annual meetings in the Conferences of Parties (COP) to assess progress on the agreement's aims. Whereas the UNFCCC was a significant first step in calling for action on the problem of climate change, it went no further than encouraging signatories to act. As a result, more than 160 nations met at COP-3 in Kyoto, Japan, in 1997 to negotiate binding limitations on greenhouse gases. The Kyoto Protocol was an update to the UNFCCC that legally bound signatories to collectively reduce worldwide emissions of six greenhouse gases (carbon dioxide, methane, nitrous oxide, sulfur hexafluoride, hydrofluorocarbons, and perfluorocarbons) by an average of 5.2% below their 1990 levels by the period 2008-2012. The treaty was opened for signature on March 16, 1998, and it came into force when at least 55 parties with at least 55% of the 1990 CO_2 emissions were represented among the ratifying parties. The agreement was activated on February 16, 2005, 90 days after it was ratified by Russia. activated the agreement. Canada's commitment to the Kyoto protocol, as per their ratification December 17, 2002, called for a reduction of domestic CO_2 emissions to 6%

below their 1990 level by the 2008-2012 interval. However, Canada's projected 2010 emissions, 828 Mt, will be 47% higher than the target of 563 Mt (Natural Resources Canada 2006).

Despite the difficulty in meeting their commitment to the Kyoto protocol, Canada has started to act on greenhouse gas emissions. The Canadian government introduced *Turning the Corner: An Action Plan to Reduce Greenhouse Gases and Air Pollution* on April 26, 2007 and pledged a 150 Mt reduction of absolute emissions by 2020. The plan proposed straightforward emissions reductions, domestic emissions trading, offsets and carbon capture and storage. Three significant developments have followed. Canada's first carbon-trading market was launched on May 30, 2008, with the opening of the Montreal Climate Exchange (CBC News 2008a). On July 1, 2008, the Province of British Columbia became the first Canadian jurisdiction to implement a carbon tax (CBC News 2008b). The tax was applied to carbon-based fuels and was initially set at $10 per tonne of greenhouse gases generated and it will rise to $30 per tonne in 2012. Lastly, the Alberta provincial government has announced $2 billion of funding for carbon storage initiatives (CBC News 2008c).

Greenhouse Gas Mitigation Strategies

There are three main approaches to addressing greenhouse gas emissions: increase energy efficiency, expand the use of low-carbon fuels and CO_2 sequestration. While increasing energy efficiency and low-carbon fuels are suitable approaches for long term mitigation of greenhouse gas emissions, CO_2 sequestration is appropriate to address the emissions from stationary point sources over the short term.

CO_2 sequestration, also termed Carbon Capture and Storage (CCS), can be divided into three approaches: geologic storage (injection of CO_2 into geological formations such as oil and gas fields, unminable coal beds and deep saline formations), ocean storage (direct release of CO_2 into the ocean water column, or onto the deep seafloor) and mineral storage (fixing CO_2 through a chemical reaction with a suitable mineral) (IPCC 2005). The carbon dioxide is first captured from a point source emitter, purified, compressed and then transported to the appropriate storage site. It is recognized that no single technology option will provide all of the necessary emission reductions and that a portfolio of mitigation measures will be required. CCS is an attractive part of that portfolio because it can directly address the emissions of existing energy generation infrastructure that is largely based on fossil fuel combustion and is expected to remain largely fossil fuel-based for decades to come.

These CCS approaches have a few disadvantages (IPCC 2005). Geological sequestration requires specific geological formations that are not found in all locations (though within 300 km of most places), includes a risk of leakage and requires ongoing monitoring. Ocean sequestration can change pH of the surrounding water which can affect marine life. Mineral sequestration is the most expensive approach (partly due to typically high temperature and pressure reaction conditions) and requires mining of suitable feedstock that subsequently needs to be disposed after it has absorbed carbon dioxide.

Carbon Dioxide Absorption By Cementitious Materials

One potential, but non-traditional, material for CO_2 sequestration is concrete. In concrete, calcium silicate cement reacts with carbon dioxide and forms carbonate products. A sequestration approach would expose the cementitious system to a much higher concentration of carbon dioxide and promote the absorption of carbon dioxide into stable carbonates. Carbonation-curing of concrete products would effectively use the concrete as a sequestration medium for captured, or recovered CO_2. This technique potentially offers safe, environmentally friendly, and permanent CO_2 storage methodology, while significantly improving early age strength (Young et al. 1974), and long-term durability of the treated concrete (Toennies and Shideler 1963).

A mechanism has been proposed for carbonation-curing (Maries 1992). The CO_2 gas must permeate through the solid and enter the aqueous pore solution. CO_2(aq) hydrates to form H_2CO_3 before ionizing to produce H+, HCO_3^-, and CO_3^{2-}. The cement phases, mainly the tricalcium silicate (alite or C_3S in cement shorthand notation) and dicalcium silicate (belite or C_2S), will rapidly, cyclically, and exothermically dissolve and release Ca^{2+} and SiO_4^{4-} ions. The carbonate phase $CaCO_3$ nucleates and precipitates as a solid phase.

The carbonation of the anhydrous phases - tricalcium silicate and dicalcium silicate - forms silicate hydrate gel, calcium carbonate and releases heat (Goodbrake et al. 1979):

$$C_3S + 3CO_2 + H_2O \rightarrow S\text{-}H + 3CaCO_3 + 347\ \mathrm{kJ/mol} \tag{1}$$

$$C_2S + 2CO_2 + H_2O \rightarrow S\text{-}H + 2CaCO_3 + 184\ \mathrm{kJ/mol} \tag{2}$$

If present in the raw materials, or as a result of hydration, lime (calcium hydroxide or CH) can be carbonated to produce calcium carbonate:

$$CH + CO_2 \rightarrow CaCO_3 + H_2O + 74\ \mathrm{kJ/mol} \tag{3}$$

Calcium silicate hydrate gel formed during hydration will also be carbonated:

$$C\text{-}S\text{-}H + 2CO_2 \rightarrow SiO_2 + 2CaCO_3 + H_2O \tag{4}$$

A relationship between the chemistry of a cementitious material and the maximum amount of CO_2 that can be combined in carbonation has been developed (Steinour 1959) assuming that all CaO (except that present as $CaSO_4$) converts to $CaCO_3$, all MgO converts to $MgCO_3$ and the alkali oxides convert to alkali bicarbonates:

$$CO_2(\%) \rightarrow 0.785\ (CaO - 0.7\ SO_3) + 1.091\ MgO + 1.420\ Na_2O + 0.935\ K_2O \tag{5}$$

This relationship suggests that the maximum CO_2 uptake (by original mass) for a Portland cement having a typical composition of 63% CaO is approximately 50%. In pure thermodynamic terms, assuming a 100% degree of carbonation, the sequestration potential of one tonne of cement would be a half tonne of carbon dioxide which equals the amount of CO_2 released from the decomposition of limestone in production of one tonne of cement.

RESEARCH OBJECTIVES

While carbonation-curing of cementitious materials has been a topic of study for over 30 years (Young et al. 1974), the previous emphasis has primarily been on taking advantage of the rapid strength development and acceleration in setting. Maximizing the carbonation uptake for sequestration purposes has not been investigated before. The technology needs to be reassessed in terms of changing motivations, resulting from the current climate change crisis.

This research project investigates the optimization of carbonation-curing of cement/slag concretes for both carbon dioxide sequestration purposes and enhanced material performance. Carbonation-curing can improve the properties of treated concrete while converting CO_2 to chemically stable $CaCO_3$, and accelerating the early age curing. The challenge is to maximize the carbon uptake and strength gain in a concrete product manufactured by an industrial production line. This research project will investigate the carbonation of cementitious materials with the objective of integrating carbon dioxide sequestration into precast concrete production.

This project represents the first step towards the implementation of carbonation-curing as a method of carbon dioxide sequestration in building products. The technique features a unique combination of environmental, technical and economic benefits. Implementation of a carbon credit trading scheme would effectively make the technology economically attractive and, perhaps, profitable. The current environmental concerns provide the motivation for investigating carbonation-curing with the goal of maximizing carbon dioxide uptake.

If carbonation-curing is to be used to produce concrete products then the incorporation of slag must be investigated. A traditional approach to lower the environmental impact of concrete is to incorporate slag as cement replacement. The current proposal for carbon dioxide sequestration in concrete products includes essential and novel research into the carbonation of slag and slag blended concretes. The use of two different slags, GGBF slag as a cement substitute and steel slag as a manufactured fine aggregate, provide two different approaches for maximizing carbon dioxide uptake. The use of GGBF slag (a waste material) to replace cement (with about 670 kg of CO_2 emissions associated with the production of every tonne) readily increases the net sequestration efficiency of a carbonated concrete by reducing the CO_2 emissions associated with the binder. The use of carbonated slag as a fine aggregate finds new use for a waste material while incorporating carbon dioxide into the aggregates. The aggregate fraction is typically 80%-90% of the solid ingredients in a typical concrete product so to use both the aggregates and the binder to absorb CO_2 is a novel approach to increasing its uptake.

The main goals of the research program are:

- To assess cementitious materials in terms of their ability to absorb carbon dioxide.

- To study the use of GGBF slag as cement replacement to reduce CO_2 emissions associated with the binder and to improve the long term performance of the slag blend concrete
- To investigate the use of a carbonated calcium-rich waste material, ladle slag from steel refining, as a fine aggregate in concrete products
- To maximize the net benefit by maximizing carbonation uptake through process conditions and the selection of materials with a low embodied CO_2
- To examine the strength and durability of carbonation-cured concrete samples that have a maximized carbon dioxide uptake
- To identify the candidate products for CO_2 sequestration, develop a beneficial use of as-captured or recovered CO_2, and estimate the scale that carbon sequestration through carbonation-curing would have in the United States and Canada.
- To perform an energy analysis and quantify the potential net gain for CO_2 sequestration in concrete products using two carbon dioxide sources: recovered CO_2 and as-captured flue gas
- To compare energy consumption involved in carbonation-curing with that by steam curing and autoclave curing

Successful application of a carbonation-curing process is considered to make low energy demands and to offer economic and performance benefits. Carbon dioxide sequestration through mineral carbonation has been extensively studied but no mineral carbonation technique has been found to be economically acceptable. Being able to prove that carbonated concrete products can be produced and offer environmental and economic advantages would inspire work towards further implementation of the idea. The biggest question is how much carbon dioxide can be incorporated into concrete products?

THESIS STRUCTURE

The research is presented as a manuscript-based thesis. After the literature review there are four sections each written as a paper that has been published, or has already been submitted to a journal for review. Each of the sections is preceded by a section that explains the context of the work within the research as a whole.

Chapter Two presents the literature review and highlights the work that has previously been done in the area of early-age carbonation of concrete. Chapter Three presents lab work that studied the carbonation of a variety of calcium rich materials. This informed the selection of appropriate materials for further study. A novel way of increasing the carbon absorption of concrete was studied in chapter four. Steel slag was carbonated and then used as a fine aggregate in both hydrated and carbonated concrete. Chapter Five examined aspects of the long-term performance, including strength and durability, of carbonation-cured and normally hydrated concretes. The sixth chapter assesses the implications of carbonation-curing concrete products with either recovered CO_2 or CO_2-rich flue gas. The energy requirements and related emissions of preparing the gas for curing are balanced against the amount of carbon dioxide that can potentially be sequestered into a variety of common concrete building products. The final chapter offers conclusions and recommendations for future work. Appendix 1 contains relevant work that could not be included in Chapter Five. Appendix 2 combines some of the work from Chapters Five and Six to draw additional conclusions.

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TABLES

Table 1.1: Greenhouse gases affected by human activities (adapted from IPCC 2007b)

	Gas				
	CO_2	CH_4	N_2O	CFC-11	HFC-23
Pre-industrial concentration*	278 ppm	715 ppb	270 ppb	0	0
Concentration* in 2005	379 ppm	1774 ppb	319 ppb	251 ppt	18 ppt
% change since 1998	+13	+0.6	+11	-5	+29
Atmospheric lifetime (yrs)	5 - 200	12	114	45	270
Radiative Efficiency ($W\ m^{-2}\ ppb^{-1}$)	1.4×10^{-5}	3.7×10^{-4}	3.0×10^{-3}	0.25	0.19
GWP†	1	21	310	3,800	11,700

* ppm – parts per million, ppb – parts per billion, ppt – parts per trillion

† Global Warming Potential, for a 100 year time horizon

Table 1.2: Profile by process or industrial activity of worldwide large stationary CO_2 sources with emissions of more than 0.1 million tonnes of CO_2 per year (adapted from IPCC 2005)

Process	Number of Sources	Total Emissions (Mt CO_2 yr^{-1})	Fraction of total
Power Generation	4,942	10,539	78.8%
Cement production	1,175	932	7.0%
Refineries	638	798	6.0%
Iron and steel industry	269	646	4.8%
Petrochemical industry	470	379	2.8%
Oil and gas processing	NA	50	0.4%
Other sources	90	33	0.2%

FIGURES

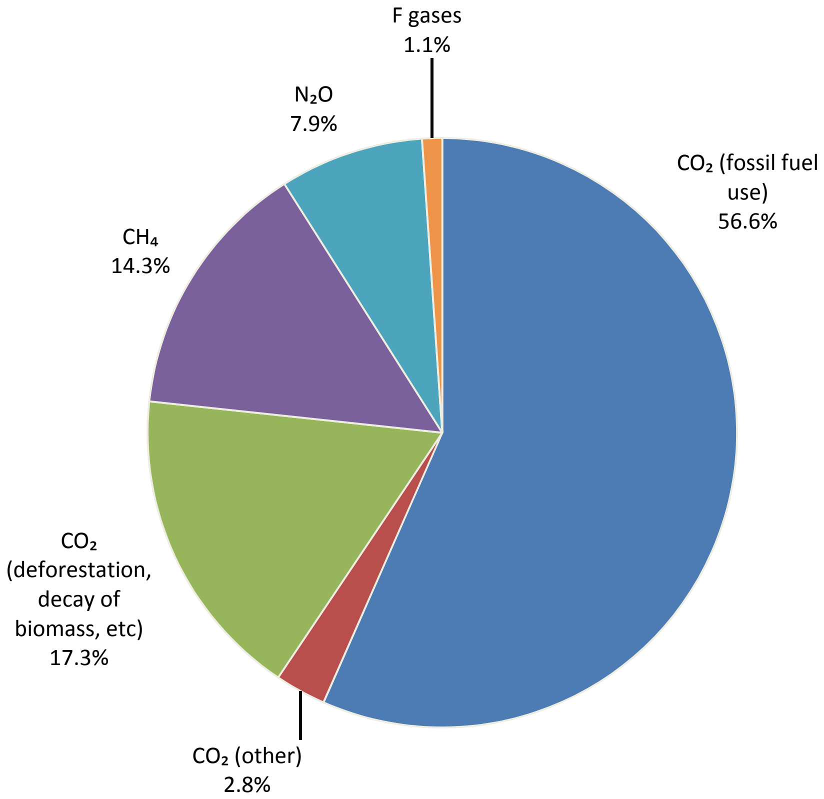

Figure 1.1: Distribution of global anthropogenic greenhouse gas emissions in 2004 (adapted from IPCC 2007a)

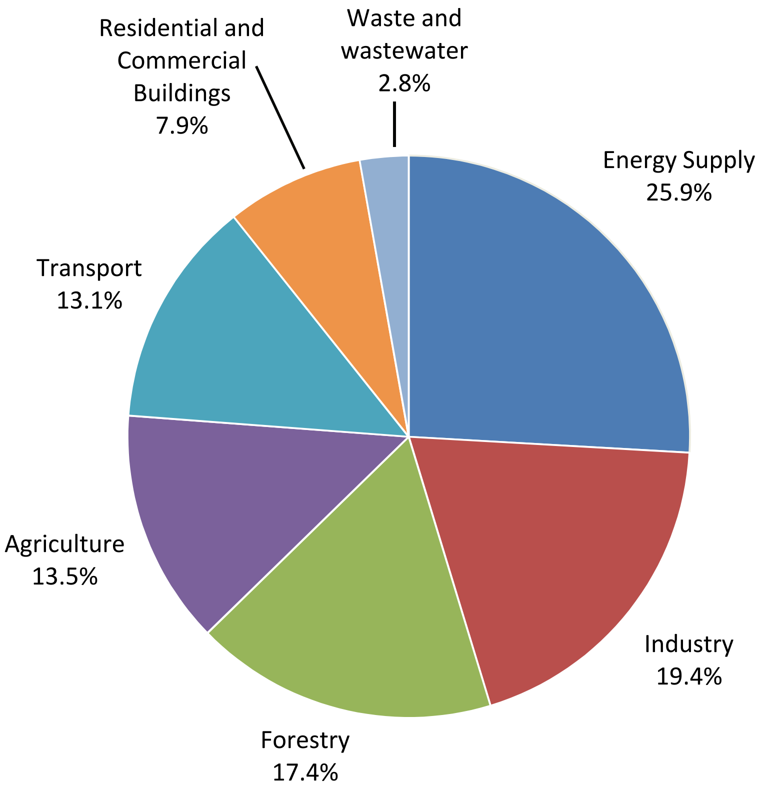

Figure 1.2: Sources of GHG emissions by sector in 2004 (adapted from IPCC 2007a)

Chapter 2

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LITERATURE REVIEW

INTRODUCTION

Carbonation is a chemical reaction between carbon dioxide and metal ions. It occurs in concrete at different ages. When fresh concrete is deliberately exposed to carbon dioxide, the carbonation can promote accelerated curing (Young et al. 1974). Early age carbonation involves the intentional exposure of prefabricated products, immediately after their forming, to high concentrations and/or pressures of carbon dioxide to bring about deliberate hardening of the sample by carbonation reactions. By contrast, if matured concrete carbonates in service, it is often referred to weathering carbonation (Neville 1996). It involves the reaction of atmospheric carbon dioxide with a mature microstructure of well-developed hydration products while the completion of the reaction would require the entire service life.

Weathering carbonation of hydrated cement paste is typically detrimental to concrete. The consumption of calcium hydroxide leads to reduction in the pore solution pH (Richardson 1988) which can lead to corrosion of the ferrous reinforcement. Atmospheric carbonation can also cause carbonation shrinkage (Powers 1962) which can lead to unstable dimensional change and cracking in restraint. The carbonation-induced corrosion of ferrous reinforcement in concrete has been extensively studied (Parrott 1987; Bertolini et al. 2004). In this context, the carbonation involves the reaction of atmospheric CO_2 with mature hydration products. The carbonation of a mature, hydrated microstructure will involve the reaction of CO_2 with hydration products. This type of reaction is the basis of atmospheric carbonation, wherein concrete products will react with the gas from the air where it has a concentration of slightly above 0.038% (Tans 2008).

The carbonation of calcium hydroxide releases 74 kJ/mol according to the following reaction (Moorehead 1986):

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

The kinetics of atmospheric carbonation are well described (Papadakis et al. 1991). C-S-H will react with CO_2 and become progressively decalcified leading to the eventual formation of silica gel (Goodbrake et al. 1979b). The carbonation of calcium silicate hydrate gel will dominate subsequent stages of carbonation (Young et al. 1974). The carbonation of the gel will produce calcium carbonate while the gel becomes progressively decalcified. The reaction can be described according to:

$$x\mathrm{CaO \cdot SiO_2} \cdot y\mathrm{H_2O} + (x-x')\mathrm{CO_2} \rightarrow x'\mathrm{CaO \cdot SiO_2} \cdot y'\mathrm{H_2O} + (x-x')\mathrm{CaCO_3} + (y-y')\mathrm{H_2O} \quad (2)$$

Ettringite will also carbonate (Grounds et al. 1988; Nishikawa et al. 1992) producing calcite, gypsum and aluminate gel as:

$$\mathrm{6CaO \cdot Al_2O_3 \cdot 3SO_3 \cdot 32H_2O + 3CO_2} \rightarrow$$
$$\mathrm{3CaCO_3 + 3CaO \cdot SO_3 \cdot 2H_2O + Al_2O_3} \cdot x\mathrm{H_2O} + (26\text{-x})\mathrm{H_2O} \quad (3)$$

The monosulphoaluminate, or AFm, phase will react with carbon dioxide according to equation 4 (Venhuis and Reardon 2001):

$$\mathrm{4CaO \cdot Al_2O_3 \cdot SO_3 \cdot 12H_2O + 3CO_2} \rightarrow$$
$$\mathrm{3CaCO_3 + CaO \cdot SO_3 \cdot 2H_2O + Al_2O_3 \cdot 3H_2O + 7H_2O} \quad (4)$$

Carbonation-curing is distinct from weathering carbonation because the carbonation reactions occur at a very early age and are used to rapidly produce useful concrete products that have a high early strength. The concept has been studied since the late 1800s (Bukowski and Berger 1979). Commercial applications of the technology have been extremely limited due to the cost of gas production, the requirement for a closed chamber and the non-uniform microstructure. However, the technology is attracting renewed interest as efforts towards reducing emissions of the most important greenhouse gas, carbon dioxide, are intensified.

Carbon dioxide is used as a raw material in several industries. These include urea and methanol production, refrigeration systems, and as an inert agent for food packaging, beverages, welding systems, fire extinguishers, water treatment processes, and horticulture (Mazzotti 2005). Carbonation-curing of cementitious building materials can serve as an industrial process to uptake CO_2 in a beneficial way. The incorporation of CO_2 emission reduction goals into a program of sustainable development will require technologies with both economical and technical benefits.

The deliberate carbonation of concrete has potential for increased and accelerated storage of carbon dioxide. When considered as a carbon dioxide sequestration methodology, carbonation-curing of cementitious products can potentially serve to reduce the net emissions from large stationary point sources. A comprehensive review of the development of carbonation-curing technology is presented in this chapter along with an examination of the role it can play in the capture and sequestration of CO_2 at present and in the future. The review does not include weathering carbonation because its reaction mechanism is different and it is effect on concrete is treated as detrimental.

DEVELOPMENT OF CARBONATION-CURING TECHNOLOGY

A large number of patents on concrete carbonation-curing have been issued over the last 100 years, involving the curing of fresh products with carbon dioxide, integration of carbonation-curing into a traditional curing scheme, or carbonation of specimens that had already been subjected to a conventional curing. A summary of the early work up to the 1970s was presented by Bukowski and Berger (1979). Developments have continued in recent years and mostly called for the use of carbon dioxide of high purity.

Carbonation-curing has been used in the development of innovative concrete products. CO_2 at 300 to 600 kPa has been used for hardening cementitious building products that are continuously extruded through a die and cut by a saw (Alpar et al. 1991). Carbonation using supercritical CO_2 (carbon dioxide above both its critical temperature, 31.1 °C, and critical pressure, 7.38 MPa) has been promoted since the gas in such a state is very dense, and it acts as a solvent to water and can penetrate very fine pores. The performance of glass fiber reinforcement has been improved by reducing the calcium hydroxide content and pH of cured concrete exposed to supercritical CO_2 (Jones Jr. 1997). Such carbonation has also been employed to create a dense cementitious product with polymeric fiber reinforcement (Knopf and Dooley 2002).

Given that the price of purified gas has been a barrier to the implementation of carbonation-curing in the past, dilute concentrations of CO_2 (such as flue gas) have been suggested. A carbon dioxide/steam mixture for curing cement and asbestos fiber blocks at elevated temperature (up to 150 °C) and pressure (up to 175 psi or 1206 kPa) has been proposed (Staley 1950). Another proposal involved the pretreatment of cement, asbestos fibers and silica blocks with dilute CO_2 (20%) at pressures up to 30 psi (or 206 kPa) to achieve an initial set and permit their safe handling before being autoclaved (Schulze 1967). The incorporation of carbonation with combustion emissions into the precuring period of steam-cured concrete was proposed (Soroushian and Hsu 1999). Combustion gas with 3 to 5% carbon dioxide has been suggested as the curing gas in a system to cure cementitious products with alternating warm (60 °C to 75 °C) and cold moist treatments (Simunic 1970). The concentration of CO_2 in flue gas varies by source and the purification of carbon dioxide from dilute gas streams becomes more difficult and less efficient as the concentration decreases. Using a dilute stream in a concrete carbonation approach would prove to be attractive.

DEVELOPMENT OF THE THEORY OF CONCRETE CARBONATION

Carbonation of Anhydrous Phases

The mechanism of the carbonation-curing of cement was systematically studied in the 1970s at the University of Illinois. The main calcium silicate phases were shown to react in the presence of water to form both calcium carbonate and calcium silicate hydrate gel (Berger et al. 1972) as:

$$3CaO \cdot SiO_2 + (3-x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_3 \cdot yH_2O + (3-x)CaCO_3 \quad (5)$$

$$2CaO \cdot SiO_2 + (2-x)CO_2 + yH_2O \rightarrow xCaO \cdot SiO_3 \cdot yH_2O + (2-x)CaCO_3 \quad (6)$$

The carbonation reaction is exothermic. The carbonation heats of reaction for the main calcium silicate phases are 347 kJ/mol for C_3S and 184 kJ/mol for β-C_2S (Goodbrake et al. 1979a). The calcium silicate hydrate (C-S-H) gel that forms is understood be intermixed with $CaCO_3$ (Berger et al. 1972). Even in an ideal case of β-C_2S and C_3S exposed to a 100% CO_2 at 1 atm (Goodbrake et al. 1979a) there is evidence of some C-S-H gel formation according to the observation that the amount of carbonate formed did not exactly correspond to the amount of calcium silicate involved in the reaction.

Since carbonation reactions proceed starting with the dissolution of carbon dioxide in water to form carbonic acid, the initial vigorous carbonation stages of carbonation can be described according to the following equation (Young et al. 1974):

$$3CaO \cdot SiO_2 + 1.2(H_2CO_3) \rightarrow 1.4CaO \cdot SiO_3 \cdot 0.6H_2O + 1.2(CaCO_3) + 0.6(H_2O) \quad (7)$$

The carbonation of calcium silicate hydrate gel will dominate the subsequent stages of carbonation (Young et al. 1974). The carbonation of the gel will produce calcium carbonate while the gel becomes progressively decalcified. The reaction can be described according to:

$$x\mathrm{CaO{\cdot}SiO_2{\cdot}}y\mathrm{H_2O} + (x\text{-}x')\mathrm{CO_2} \rightarrow x'\mathrm{CaO{\cdot}SO_3{\cdot}}y\mathrm{H_2O} + (x\text{-}x')\mathrm{CaCO_3} + (y\text{-}y')\mathrm{H_2O} \qquad (8)$$

The non-hydraulic (that is, not reactive with water) calcium silicate phases of γ-Ca_2SiO_4 and $CaSiO_3$ have also been found to react with carbon dioxide (Bukowski and Berger 1979) while the calcium aluminate phases of $Ca_3Al_2O_6$ and $Ca_{12}Al_{14}O_{33}$ (or C_3A and $C_{12}A_7$, respectively) were found to be unreactive to carbon dioxide (Berger and Klemm 1972).

The overall series of steps that occur during the carbonation-curing of a cementitious material have been summarized (Maries 1992) as follows:

1. Diffusion of CO_2 in air.
2. Permeation of CO_2 through the solid.
3. Dissolution of CO_2(g) to CO_2(aq).
4. Hydration of CO_2(aq) to H_2CO_3. This can be a slow, rate-determining step.
5. Ionisation of H_2CO_3 to H^+, HCO_3^-, CO_3^{2-}. This takes place almost instantaneously, lowering the pH locally by 3 or more units, typically from 11 to 8.
6. Cyclic, rapid, exothermic and extensive dissolution of cementitious phases C_3S and C_2S. The calcium silicate grains are covered by a loose layer of C-S-H gel, which is quickly dissolved, releasing Ca^{2+} and SiO_4^{4-} ions. The reaction of C_3A is minimal, perhaps due to a tight alumino-sulphate/carbonate coating.
7. Nucleation of $CaCO_3$ and C–S–H. Nucleation is promoted by increasing the temperature and using fine particles that act as heterogeneous nuclei.

8. Solid phases precipitate. The metastable calcium carbonate polymorphs of vaterite and aragonite can form, but eventually they revert to calcite. The final products can be amorphous.
9. Secondary carbonation. C–S–H gel that forms at an early stage can react with CO_2. The gel is progressively decalcified leading to the formation of $CaCO_3$ intermixed with silicate hydrate gel.

Carbonation of calcium silicate powders had been suggested to follow a decreasing-volume, diffusion controlled kinetic model (Goodbrake et al. 1979a) although an alternate interpretation (Knudsen et al. 1980) noted possible that phase boundary control.

The products of carbonation are generally identified as calcite though calcium carbonate occurs in three polymorphs: the stable form of calcite and the two metastable forms of aragonite and vaterite (in order of decreasing stability). The $CaCO_3$ polymorph aragonite tends to form when the material dries out while being carbonated (Goodbrake et al. 1979b) or may be the favoured product from the carbonation of β-C_2S (Goto et al. 1995).

In addition to calcium carbonate, it has also been suggested (Goto et al. 1995) that basic calcium carbonate (BCC: $2CaCO_3{\cdot}Ca(OH)_2{\cdot}1.5H_2O$) and amorphous basic calcium carbonate (ABCC: $Ca_3(OH)_{6x}(CO_3)_{3-3x}{\cdot}3yH_2O$) were among the products when C_3S, β-C_2S, and γ-C_2S are carbonated. Furthermore, in the case of magnesia-based cements (Pearce 2002), or a slag with a high MgO content, magnesite, $MgCO_3$, can be a major product.

Factors Influencing Carbonation

The extent of carbonation has been studied primarily in the context of accelerated tests used to simulate weathering carbonation. The main factors influencing the extent of carbonation-curing are the nature of the reacting material, the physical characteristics of the solid and the exposure conditions for the carbonation (Fernandez Bertos et al. 2004). Firstly, the chemistry of the binder must be reactive to CO_2. Secondly, the free water content must be sufficient to allow the carbonation reaction to proceed, however too much water can block the pore structure and prevent gas penetration. Thirdly, the porosity and permeability of the material to CO_2 are related to the compaction pressure and gas diffusion can be hindered if they are too low. Lastly, the carbonation rate increases with CO_2 partial pressure and can be increased with gas pressure.

TECHNIQUES TO QUANTIFY CO_2 UPTAKE

Defining CO_2 Uptake By Concrete Products

Determining the carbon dioxide absorption resulting from carbonation-curing depends upon the definition employed. Degree of carbonation, D_c, (Matsushita et al. 2000) is a useful concept and can be calculated based on C_0, C and C_{max}, or the initial, final and theoretical maximum CO_2 content of the material, respectively

$$D_c(\%) = \frac{C - C_0}{C_{\max} - C_0} * 100 \tag{9}$$

The theoretical maximum uptake C_{max} of a cementitious material with carbon dioxide is related to the material chemistry. The Steinour equation (Steinour 1959) expressed the theoretically possible mass gain for total carbonation at one atmosphere pressure of CO_2:

$$CO_2\,(\%) = 0.785\,(CaO - 0.7\,SO_3) + 1.091\,MgO + 1.420\,Na_2O + 0.935\,K_2O \tag{10}$$

The relationship assumes that all calcium that is not already combined with SO_3, will react with CO_2 as will all MgO and the alkalis Na_2O and K_2O. The theoretical mass gain of a typical cement that is completely carbonated would be about 50%

Carbonation uptake can also be simply defined as the percent mass gain. Whereas many other assessment techniques only use a small, point-based sample of a specimen, the mass gain is able to consider an entire specimen. The mass gain of a carbonated sample has been determined by removing the free water by drying at 60 °C to constant weight (Johnson 2000) and comparing this residual sample mass to the original sample mass. The carbon dioxide uptake can then be expressed as the mass increase in terms of the original amount of binder.

$$Mass\ gain\ (\%) = \frac{Mass_{sample,\ final,\ dried\ at\ 60°C} - Mass_{sample,\ initial}}{Mass_{dry\ binder}} = \frac{\Delta Mass}{Mass_{dry\ binder}} \qquad (11)$$

This approach assumes that any mass change is associated with the binding of CO_2. The assumption, that the mass gain by hydration is insignificant, is not necessarily valid if hydration accompanies the carbonation.

Uncertainties related to the mass gain associated with bound water can be eliminated if the mass gain relationship considers a closed system (Monkman and Shao 2006). If all of the water present at the beginning of the test is accounted for at the end of the test (by weighing an undried sample and collecting any water expelled from the sample) then the difference in the system mass between the initial and carbonated states would represent the mass of CO_2 added to the system.

$$Mass\ gain\,(\%) = \frac{\left(Mass_{final} + Mass_{water\,loss}\right) - Mass_{initial}}{Mass_{dry\,binder}} = \frac{\Delta Mass}{Mass_{dry\,binder}} \qquad (12)$$

The numerators in the three definitions are related to carbon dioxide uptake expressed by a mass increase due to carbonation and represent a similar physical quantity. However, the denominators used as references are quite different. In Equation 9, the denominator represents the maximum increase in CO_2 concentration (based upon the binder chemistry) and the formula determines the degree of carbonation. The denominator of Equations 11 and 12 uses the amount of binder. The evaluation of uptake is easier when it is based upon the binder content than upon the CaO content. The maximum mass gain of a Portland cement binder is approximately 50% and, therefore, the degree of carbonation, calculated by Equation 9, would be about twice the corresponding mass gain as determined by Equations 11 or 12.

To quantify CO_2 uptake, a number of experimental techniques can be used, including methods of mass gain, thermogravimetry, quantitative XRD, chemical analysis, and infrared spectroscopy.

Thermogravimetry

Thermogravimetry has been a common approach for the quantification of carbonates. Both constant temperature pyrolysis and dynamic TGA have been employed successfully. It is important factor to consider the temperatures at which the various thermal decompositions will occur. The interpretations of the mass loss data vary but in a general approach, the mass loss between 600 °C and 800 °C can be interpreted as the loss of CO_2 from calcite (Matsushita et al. 2000). Free water is released at temperatures below 105 °C while combined water (hydration products) has been associated with mass losses up to 400 °C (Johnson 2000).

Some approaches recognize the evolution of carbon dioxide at temperatures below 600 °C. $MgCO_3$ decomposes between 300 °C and 350 °C (Knopf and Dooley 2002). Poorly crystalline carbonate phases decompose between 200 °C and 600 °C and decarbonation of well formed calcite, vaterite and aragonite crystals occurs at higher temperatures (Goto et al. 1995). Other researchers studying the carbonation of calcium silicate hydrates (Cole and Kroone 1959), or $CaSiO_3$ and γ-$2CaO \cdot SiO_2$ (Bukowski and Berger 1979), have associated the decomposition of small, poorly crystalline calcium carbonates with mass loss between 350 °C and 600 °C.

Another approach has suggested that carbon dioxide mass loss can be divided into three types (Kroone and Blakey 1959). Unstable carbon dioxide (from calcite intimately associated with silica) is lost below 500 °C, stable carbon dioxide (from calcite sufficiently separated from silica to behave as pure calcite) is evolved between 500 °C and 700 °C, while carbon dioxide associated with alkali metal carbonates is released above 700 °C.

A constant temperature pyrolysis approach (Goodbrake et al. 1979a) interpreted the mass losses below 105 °C as uncombined water, 105 °C to 350 °C as combined water, and 350 °C to 1000 °C as the decomposition of carbonates with the latter mass loss equal to the mass of CO_2. Other researchers have suggested a possible overlap in mass losses with the possibility that combined water would be lost up to 400 °C, while CO_2 can be evolved at temperatures as low as 325 °C (Bukowski and Berger 1979). One limitation of constant temperature pyrolysis is that sulfides, that are often present in ground granulated blast furnace slag, can gain mass as they oxidize to form sulfates (Legodi et al. 2001). Therefore, the data must be interpreted carefully to allow for this phenomenon.

It has been suggested that, for dynamic TGA analysis, the derivative thermogravimetric curve can be used to identify the precise onset and end temperatures for mass loss reactions observed on the TGA curve (Kneller et al. 1994). Quantification of the carbonate content would then result from an interpretation of the sample at hand rather than by strict adherence to the mass loss over broad temperature ranges.

Quantitative XRD

Quantitative XRD has made use of internal standards such as 25% TiO_2 (Goodbrake et al. 1979a) which was used to determine the reaction degree based upon peak analysis. Alternately, $Mg(OH)_2$ has been used (Berger et al. 1972) to quantify carbonation by comparing the 2.20Å peak of $3CaO \cdot SiO_2$ and the 1.58Å peak of $Mg(OH)_2$ to the 1.88 Å peak of $CaCO_3$. The modern approach to QXRD involves the Rietveld method which utilizes a least squares approach to determine a theoretical line profile that best matches a measured profile. For carbonation, the quantification of calcite using the Rietveld method has been found to be comparable to both the calcimetric method or the TG/DSC method (Gualtieria et al. 2006).

Evolved Gas of a Heated or Acidified Sample

Carbonate content can be quantified by measuring the gas evolved from a heated or acidified sample. Gravimetric methods measure the mass gain of an absorbent. Examples include capturing CO_2 evolved from a heated sample in an ascarite/dehyrdite mixture (Kroone and Blakey 1959), or decomposing a sample in hydrochloric acid and capturing the liberated CO_2 in an absorption bulb containing ascarite (ASTM 2006). Evolved CO_2 can be captured in a standard barium hydroxide solution, whereupon it can be quantified through titration with HCl (Schollenberger and Whittaker 1958). A direct volumetric measurement of carbon dioxide evolved upon heating a material with a mixture of potassium sulphate and sulphuric acid has been used (Bessey 1939). The volume of CO_2 evolved from an acidified sample has also been measured by collecting it in an inverted and submerged buret (Pile et al. 1998). Quantifying evolved gas through gas chromatography has been found to be very sensitive and thus appropriate for low carbonate contents or small sample sizes (Carpenter 1962). The thermal conductivity of the evolved gas can also be used to quantify CO_2 content (Thomas and Hieftje 1966). Disadvantages of gas measurements include their complexity, time consuming nature, and requirements for specialized equipment. Acid-based techniques also cannot guarantee that all of the carbon dioxide in the sample is actually released and can, in the presence of mineral additions such as ground granulated blast furnace slag, possibly form additional gaseous species (such as H_2S) that add uncertainty to the calculated carbonate values.

Infrared (IR) based Carbon Analysis

Infrared spectroscopy (IR) can be used to quickly quantify evolved carbon dioxide through its characteristic infrared absorption wavelengths (Pobiner 1962). Fourier Transform Infrared Spectroscopy (FT-IR) (Legodi et al. 2001) has been used to distinguish between various polymorphs (calcite, aragonite, vaterite) of calcium carbonate (Vagenas et al. 2003). While such approaches are accurate, they require expensive and complex analytical equipment and may not be ideal for all situations or environments.

Reported Uptake of CO_2 by Carbonation-Curing

There is little data concerning the quantification of carbon uptake of cementitious material carbonation-cured in experimental settings. Relevant instances are summarised below.

Blends of cement, slag and solidified hazardous waste have been formed into compacts (compaction load 1 MPa, 20 × 10 mm cylinders) and treated with CO_2 at atmospheric pressure for 100 minutes (Lange et al. 1996b). The CO_2 contents of compacts were less than 6% (by weight of solids), but they increased by 3 to 6% with the addition of the waste.

The CO_2 uptake of cement/steel slag compacts (28 mm diameter × 28 mm high, compaction load 0.5 MPa) exposed to 3 bar (300 kPa) CO_2 for one hour reached up to 15% (thermogravimetric mass loss between 400 °C and 800 °C, by the original mass of binder) (Johnson et al. 2003a). A claim that this represents an 18% uptake by mass of the original binder must be tempered, however, given that this does not take into consideration the fact that thermograviemtric mass loss of the uncarbonated the control was 5%. The actual carbonation mass uptake was likely about 10 to 11%.

The exposure of cement paste (formed with a compaction load of 14 MPa) to atmospheric CO_2 for 30 minutes resulted in a carbonation uptake of about 10% by sample weight of the cement. A similar test of a 50/50 cement/sand compact resulted in a CO_2 uptake of 6.8% (by weight of the cement in the mortar) (Wagh et al. 1995).

Compacts of milled autoclaved lightweight concrete dust (100 × 100 × 12 mm thick, compaction load 30 MPa), carbonated with dynamically flowing carbon dioxide for durations of 24 hours, achieved a maximum mass fraction of 14% CO_2 (Liu et al. 2001). The recycled waste, in this case, included C-S-H gel and tobermorite rather than anhydrous cementitious phases.

Specimens of cement and wood fiber reinforcement (50 mm diameter × 12 mm thick) carbonated with 7 bar (700 kPa) carbon dioxide for up to 180 minutes reached a CO_2 uptake of 13% (Simatupang and Habighorst 1992). The basis of evaluation of carbon content was not clarified.

Most carbonation-curing approaches have been limited to under 12% mass gain (about 24% of the total possible carbonation reaction). Thus, it is evident that carbonation-curing has been unable to achieve as complete carbonation as what can be found in long term reactions or the high temperature/high pressure mineral carbonation approaches.

Several limits to the reaction have been identified. Since the carbonation reaction requires water to proceed, water starvation, relating to the water loss due to exothermic temperature rise, has been identified as an important limiting factor (Berger et al. 1972; Young et al. 1974; Hannawayya 1984). Other possibilities include carbonation products filling the pores and restricting gas ingress (Bukowski and Berger 1979) or the build up of products to the extent that they coat the reacting particles or block the reaction sites (Shih et al. 1999).

Sorochkin et al. (1975) showed that uptake and carbonation degree depend on the water to binder ratio (w/b) selected and the compaction pressure. Therefore, for each application and mix design there will be an optimal w/b and compaction pressure that will provide the best uptake results. These optimized factors may not necessarily be consistent with traditional operation which add an additional difficulty for the integration of carbonation-curing in, as opposed to pursuing it as a replacement for, a traditional accelerated curing scheme.

The use of dilute gas provides results comparable to using pure gas but with a lower rate of reaction that limits the exothermic temperature rise, and thereby allows more thorough penetration (and reaction) of CO_2 gas (Soroushian et al. 2003).

PERFORMANCE OF CARBONATED MATERIALS

Early Strength

The carbonation of suitable cementitious materials has shown that strength development can be achieved within minutes. C_3S and β-C_2S mortars carbonated for 81 minutes had more than 3 times the strength of a comparable mortar hydrated for 24 hours (Young et al. 1974). One optimized carbonation of a cement mortar was found to achieve a higher strength after 5 minutes of carbonation than after 24 hours of hydration (Klemm and Berger 1972). For mortar subjected to a vacuum curing carbonation (Hannawayya 1984), which allows higher w/b to be used when creating products, the strength of a sample carbonation-cured 38 minutes had a higher strength than samples hydrated for 7 and 28 days in air. For vacuum-dewatered lightweight aggregate concrete (LWAC) Malinowski and Rodhe (1983) observed that up to 45% of the 28 day strength could be achieved with 15 minutes of carbonation, with the 28 day strength equalling the 28 day strength of normally cured vacuum-dewatered concrete. Cement compacts carbonated for as little as 30 minutes have been found to reach the ASTM requirement for 28 day strength of Portland cement (Wagh et al. 1995).

Late Strength

The effect of rapid early strength gain on the late strength development has not received adequate attention. The limited reports have shown contradictory results. Exposure to carbon dioxide in the initial stages of curing does not interfere with subsequent hydration of the paste specimens with the carbonated samples having higher strengths up to 28 days (Sorochkin et al. 1975). The strength of carbonation-cured mortars has been found to increase when subjected to subsequent hydration to the extent that it was 50% stronger than samples hydrated for three days

(Klemm and Berger 1972). However, the strength development was found to reach a maximum and the strength of the carbonated sample was exceeded by that of a normally hydrated specimen at 14 days. Carbonation was found to result in an autoclaved strength that was 40-60% higher than that of an uncarbonated mortar. Hannawayya (1984) found that the strength of a mortar carbonated for 38 minutes was higher than that of mortars hydrated in air for 7 and 28 days. However, after the carbonated sample was hydrated in air for 7 and 28 days, the strength progressively decreased. Hydration in water, rather than in air, reduced the strength decrease. The carbonated microstructure was observed to have incorporated new calcium hydroxide crystals with hydration time and have become weaker.

Durability

Carbonation can reduce the occurrence of efflorescence by either consuming or preventing the formation of calcium hydroxide. Carbonated concrete products have shown a lower tendency to develop efflorescence (Weber and Matthei 1941). Accelerated curing procedures (such as steam-curing or vapour-curing) have been known to include combustion exhaust in the curing atmosphere to introduce some carbonation during the curing with the expressed intention of reducing efflorescence.

Carbonation-curing of materials, after they have set, has been studied for several purposes. CO_2 has been used to dry and preshrink cured masonry units (Leber and Blakey 1956; Polisner 1956; Toennies 1960; Toennies and Shideler 1963; Freedman 1969), to reduce their carbonation shrinkage in-service. While the maximum carbon dioxide sequestration might not necessarily be achieved by carbonating a concrete sample that has already been cured, the acceptance of integration of carbonation into the curing process is an important aspect.

Other durability issues (such as permeability, freeze/thaw performance, resistance to sulphate attack) have not been well studied. These issues are important concrete durability aspects in many service environments and require attention.

Uses of Carbonation-Curing

Carbonation is known to accelerate hardening of cement products reinforced with wood fibres (Schmidt 1988; Hermawan et al. 2002; Soroushian et al. 2003). It helps to solve the compatibility problem of wood with cement. The potential exists to optimize this process for carbon dioxide uptake.

Carbonation of concrete has been studied as a method of waste stabilisation (Fernandez Bertos et al. 2004). Waste materials may be mixed with the concrete and the carbonation process reduces both the permeability of the concrete and the leaching potential of the contained wastes. The stabilisation of a waste solution in a cementitious form using either supercritical (Venhuis and Reardon 2003) or vacuum carbonation (Venhuis and Reardon 2001) has been studied. Sewage sludge-cement-sand mortars containing heavy metals (Valls and Vàzquez 2001) have been stabilised by carbonation. Carbonation has been found to improve the immobilisation of zinc, nickel, and arsenic (Lange et al. 1996a), chromium (Johnson et al. 2003b), and strontium (Walton et al. 1997) contained within cementitious materials. Observations showed that the carbonation products can offer both physical immobilisation and chemical encapsulation of the wastes.

Carbonation has been employed to deal with cementitious wastes. Carbonation-cured waste autoclaved lightweight concrete powder has been examined for use as the basis of an interior wall building material (Teramura et al. 2000). Carbonation-curing has been used to make compacts out of autoclaved lightweight concrete (ALC) dust, while incorporating short polymer fiber reinforcement (Hashida et al. 1996).

Slag from a steelmaking process has been made into 1 m^3 blocks and carbonated using water saturated CO_2 flowing through the block for 12 days. The blocks were sufficiently strong to be handled with heavy machinery and were considered for use as a seaweed base in the ocean (Isoo et al. 2000; Isoo et al. 2001). Compacts of stainless steel slag have been carbonated to increase their strength and decrease the leaching of metals contained therein (Johnson et al. 2003b) allowing for more effective disposal of wastes.

A sequestration methodology has been proposed whereby CH and CaO are dissolved from concrete wastes or slag and then reacted with CO_2 in ambient air (Stolaroff et al. 2005). Steel slag has been identified as an appropriate feedstock for a mineral carbonation in an aqueous suspension, at 19 bar (1900 kPa) CO_2 pressure and 100 °C (Huijgen et al. 2005). While the latter two approaches involve carbonation of cementitious materials, they can be considered straightforward mineral carbonation sequestration ideas because they bind carbon dioxide in finely ground reactive materials rather than in a construction product.

USE OF GGBF SLAG IN CONCRETE

Ground granulated blast furnace (GGBF) slag is a widely used cement replacement material. It is a by-product of iron manufacturing with a secondary cementitious nature. The many benefits of using GGBF slag in concrete include (Siddique 2008):

- Increased strength and durability, decreased permeability
- High resistance to chloride penetration, sulphate attack and alkali-silica reaction (ASR)
- Very low heat of hydration

- Suppresses efflorescence
- Improvement of life cycle costs of concrete structures
- GGBF slag is a waste product and is not associated with any primary CO_2, SO_2 or NO_x.

One issue of concrete containing GGBF slag as a cement replacement is that the early strength development over the first few days is slower for concrete with slag than without slag (Hogan and Meusel 1981; Roy and Idorn 1982). However, the strength of the slag-blended concrete can eventually exceed that of the ordinary cement concrete at later ages, typically beyond 28 days.

It is known that blended slag cement concretes, exposed to weathering carbonation, have been associated with higher carbonation rates (Osborne 1999), which can lead to lower compressive strengths (Sulapha et al. 2003). However, the study of early age carbonation of slag is very limited and has not considered the performance of carbonation-cured slag/cement blend concretes. The slow early strength development of traditionally hydrated GGBF slag blended concretes could possibly be improved through carbonation-curing.

FUTURE IMPLEMENTATION

The development and creation of zero-emissions power plants (ZEP) will create a platform and the infrastructure necessary for carbon capture with the intention of passing the carbon dioxide towards some storage methodology. If a high concentration CO_2 gas is the by-product of power generation, then the largest barrier to carbonation-curing, which is an economical supply of carbon dioxide, will be eliminated. ZEP have a great potential for the reduction of carbon dioxide gas emissions (Corradoa et al. 2006) although it is necessary to include a carbon capture step. The capture of CO_2 is intended to allow for its purification and subsequent sequestration and integration of carbonation-curing would depend on the ZEP approach being utilised. If a mixture of CO_2 and steam results from the combustion step (Griffin et al. 2005), then such gas could be ideally suited for carbonation-curing. On the other hand, if the CO_2 is captured by a CaO sorbent (Corradoa et al. 2006), then it is plausible, given earlier attempts to use flue gas as a carbonation-curing gas (for drying or strength development purposes) (Polisner 1956; Toennies 1960; Simunic 1970), that a carbonation-curing process could be integrated into a carbon capture system by using concrete as the sorbent rather than CaO which is subsequently calcined to purify the captured CO_2 for recovery.

CONCLUSIONS

Carbonation-curing is appropriate for many cementitious materials with a variety of production methods and end uses. Historically, carbonation-curing of cementitious building products has focussed on accelerating strength development, but it can be reconsidered today with a new emphasis on carbon dioxide sequestration. It is a versatile technology that is applicable to many types of products including innovative construction materials. The development of carbonation-curing for carbon storage and capture holds enormous potential for finding a new and useful approach to mitigating carbon dioxide emissions. The technique of carbon dioxide sequestration in concrete building materials has not been investigated.

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Chapter 3

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ASSESSING THE CARBONATION BEHAVIOUR OF CEMENTITIOUS MATERIALS

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Sean Monkman and Yixin Shao

PREFACE

The presented work that follows covers the preliminary assessment of the carbonation of cementitious materials. The research began by examining the carbonation potential of a variety of typical calcium-rich materials. The selected materials were considered to be both widely available and economical.

Three traditional cementitious materials studied were a normal Portland cement (Canadian Type 10), a high early strength cement (Type 30) and a ground granulated blast furnace slag. Two calcium-rich waste materials that are not typically employed in concrete, Electric Arc Furnace (EAF) slag and high carbon fly ash, were also considered. Calcium hydroxide, while not being practical for large scale use as a construction material, was tested to examine a material that has a very high potential to absorb CO_2. The study of the conventional materials is necessary for providing the basis of carbonated concrete products while the study of the non-conventional materials assesses if the novel carbonation-curing approach can be applied to, and would be suitable for, calcium-rich materials beyond those typically used in concrete products.

This preliminary study led to a subsequent research on the development of carbonated steel slag sand to enhance the sequestration potential by concrete and of a slag cement concrete using a blended binder to reduce cement content and improve net carbonate gain.

The work is presented here, with minor non-technical edits, as it was published in the ASCE Journal of Materials in Civil Engineering, Vol. 18, No. 6, December 1, 2006. doi:10.1061/(ASCE)0899-1561(2006)18:6(768)

ABSTRACT

The carbonation behavior of six cementitious materials was examined (CSA Type 10 cement, CSA Type 30 cement, fly ash, ground granulated blast furnace (GGBF) slag, electric arc furnace (EAF) slag and hydrated lime) for applicability to CO_2 sequestration applications. No-slump press formed compacts and loose powders were subjected to 100% CO_2 at a constant pressure of 5 bar for 2 hours. The CO_2 contents of the as-received and the carbonated materials were measured. It was found that the cements, fly ash and electric arc furnace slag could each show CO_2 uptake on the order of 12% while the lime achieved nearly 40%. The blast furnace slag managed 7% uptake. The carbon uptakes achieved were significantly lower than the theoretical maximum as determined by chemistry. The two-hour carbonation produced high early age strength in cements and hydrated lime which can be used as structural materials. The strength gain in fly ash, EAF slag and GGBF slag was nevertheless not sufficient. XRD analysis determined that the primary carbonation product formed was calcite while C_3S, C_2S, C-S-H and CH were the phases consumed. SEM observations considered the morphology of the carbonation products and the degree of reaction in terms of microstructural characteristics.

INTRODUCTION

Carbonation-curing of concrete products is an accelerated curing process that injects CO_2 gas into a curing chamber at room temperature, diffuses the carbon dioxide into the fresh concrete under low pressure, and transforms the gaseous CO_2 into solid calcium carbonates ($CaCO_3$). Using mixes with low water-solids ratios and using carbon dioxide under pressure allows the gas to penetrate into and react with the calcium compounds causing rapid strength gain (Bierlich 1969). The advantages of carbonation-curing include improved dimensional stability, increased impermeability and strength; enhanced chemical and efflorescence resistance with reduced time and energy demands for production (Soroushian and Hsu 1999).

The carbonation of calcium-carrying materials forms thermodynamically stable calcium carbonates. Calcium silicate compounds can be carbonated according to the following reactions(Young et al. 1974):

$$3\ CaO \cdot SiO_2 + 3\ CO_2 + \mu H_2O \rightarrow SiO_2 \cdot \mu H_2O + 3\ CaCO_3 \qquad (1)$$

$$2\ CaO \cdot SiO_2 + 2\ CO_2 + \mu H_2O \rightarrow SiO_2 \cdot \mu H_2O + 2\ CaCO_3 \qquad (2)$$

Calcium hydroxide will also carbonate, following the reaction:

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ H_2O \qquad (3)$$

Eqs. (1) to (3) suggest that carbonation-curing is a CO_2 consuming process. In general, carbon dioxide can be sequestered into almost all compounds of calcium and converted to stable calcium carbonates. The calcium compound technology is similar to the magnesium based technology which employs the natural magnesium-bearing rocks, such as serpentine, as alkaline earth metal for carbonate formation (Blencoe et al. 2003). However, a calcium based approach to

CO_2 sequestration can be integrated into the mass production of calcium based building products and can show environmental, economical and technical benefits while offering a global CO_2 sequestration response.

The focus of current work is to investigate carbonation-curing of calcium-carrying cementitious materials to sequester CO_2 while also developing high early age strength for building materials applications. CO_2 uptake is quantified by infrared analysis and direct mass gain. The reaction is characterized by examining the carbonated materials using XRD and SEM

The Steinour formula (Steinour 1959) determines the theoretical maximum CO_2 uptake based upon the chemical composition of a material:

$$CO_2\ (\%) = 0.785\ (CaO - 0.7\ SO_3) + 1.091\ MgO + 1.420\ Na_2O + 0.935\ K_2O \qquad (4)$$

This relationship would suggest that the maximum CO_2 uptake for a Portland cement of typical composition of 63% CaO is on the order of 50%. In these terms, assuming a 100% degree of carbonation, the sequestration potential of one tonne of cement would be a half tonne of carbon dioxide. This efficiency means that the carbon dioxide released from decomposition of limestone during cement production can be totally sequestered into the concrete products and converted to solid, stable and strength-contributing calcium carbonates.

EXPERIMENTAL

The six materials used in the testing were two different cements (CSA Type 10 and CSA Type 30), a ground granulated blast furnace slag, an electric arc furnace (EAF) steel slag, a fly ash and a hydrated lime ($Ca(OH)_2$, hereafter referred to as lime). The chemical compositions of these materials as determined by XRF can be seen in Table 3.1. The two cements have nearly identical chemical compositions but the Type 30 has a Blaine fineness of 469 m^2/kg compared to 373 m^2/kg for the Type 10 cement.

The mix design of a single three sample batch consisted of 720 g of binder and 108 g of water (w/s = 0.15) for all materials except for the fly ash which required more water for press-forming (w/s=0.2). It has been noted that maximum carbonation weight gain occurs at a range of different w/s for different materials and this optimum level lacks a simple relationship with sample chemistry (Johnson 2000). The chosen w/s of 0.15 has been identified (Goodbrake et al. 1979a; Goodbrake et al. 1979b) as being the optimum, in terms of promoting the carbonation reaction, for carbonation-curing of C_3S and very close to optimum for carbonating C_2S.

The water and binder were mixed with a mechanical mixer for approximately 90 seconds. For each of three samples, approximately 270 g of the mixture was made into a 76 mm by 127 mm compact sample using a compaction force of 79 kN (corresponding to a pressure of 8 MPa). The thickness of the compacts depended on the compressibility of the material used but was no less than 13 mm.

Figure 3.1 shows the process schematic. The samples were placed into the chamber which was then evacuated to about 50 kPa (0.5 bar) below atmospheric pressure to remove the air. The specimens were then exposed to CO_2 for 2 hours at 500 kPa (5 bar). The gas was heated as it went between the gas cylinder and the chamber in order to minimise the cooling effects of the uncompressed CO_2. A carbon dioxide gas of 99.5% purity was used to simulate CO_2 recovered from flue gas at point sources such as thermal power plants or cement plants. A constant supply of gas maintained the chamber pressure and ensured that any carbon dioxide consumed by reaction was replaced. A small indentation (approximately 3 mm deep) was made in the edge of one of the three specimens to allow the insertion of a thermocouple. The temperature, pressure, initial and final mass of the specimens, and the mass of water condensed on the walls of the chamber were recorded.

Carbonation was repeated using the material in bulk powder form using an amount equivalent to one compact sample (240g of binder and 36g of water). It was assumed that the porosity of the samples in an uncompacted powder form would be much greater than that of the compact samples and thus display a higher CO_2 uptake if porosity was a controlling factor.

The two cements were also used to make hydrated compact samples for reference. After being press-formed and subjected to 24 hours initial curing in a sealed plastic bag, the hydrated compacts were placed in a moist environment for further curing. The modulus of rupture (MOR) and compressive strength of the carbonated specimens were tested immediately upon completion of the two-hour carbonation. MOR was obtained by breaking the specimen in a three-point bending test with a span of 101.6 mm. The bending test split one specimen into two halves which were then tested in compression across an area about 63 mm times a thickness. The hydrated samples were tested at an age of 7 days. For each batch, at least three specimens were tested for average. Powder samples, for CO_2 content and carbonate analysis, were collected from the fractured specimens by drilling on the surface (to depths less than approximately 2 mm) and in the core of the specimens. The powder was ground in a mortar and pestle and sieved to pass a 106 μm sieve. The powder was subjected to XRD analysis employing a Philips PW1710 Powder Diffractometer (Cu Kα radiation, scan interval 5-60° 2θ, 0.02° and 0.5 s per step). The fracture surfaces of the specimens were analyzed by scanning electron microscopy employing a JEOL JSM-840A with an EDAX Phoenix EDS microanalysis system.

The CO_2 contents of the carbonated samples were quantified using an automated ELTRA CS-800 analyser with an induction furnace and infrared detection. Powder samples collected from surface and core were tested separately to investigate their differences in carbonation. The instrument was calibrated using cement reference materials and synthetic carbonate standards. The basis for this measurement is:

$$CO_2 content\ (\%) = \frac{CO_{2\,evaparated\,@1000^\circ C}}{Total\ mass\ after\ carbonation} \tag{5}$$

These data were used to calculate a carbonation degree, D_c, based on C_0, C and C_{max}, the initial, final and theoretical maximum CO_2 content of the material, respectively (Matsushita et al. 2000):

$$D_c(\%) = \frac{C - C_0}{C_{\max} - C_0} * 100 \tag{6}$$

Another estimate of the carbonation was made by considering the change in mass of the sample. CO_2 uptake estimated by mass gain is determined by considering the initial mass (made up of dry binder and mix water), the final carbonated mass (including the lost water) and the original mass of the dry binder:

$$Mass\ gain(\%) = \frac{(Mass_{afterCO2} + Water_{lost}) - Mass_{beforeCO2}}{Mass_{dry\ binder}} = \frac{\Delta Mass}{Mass_{dry\ binder}} \tag{7}$$

The water is included in this calculation because this is treated as a closed system in that the only water present at the end of the test was present in the chamber at the beginning of the test as either mix water or water chemically combined in the sample (in a phase such as calcium hydroxide). If the assumption holds that the increase in mass during the carbonation was due only to the incorporation of carbon dioxide into solid products then this can provide an alternative estimate of CO_2 uptake. The CO_2 content by Eq. (5) is based upon analysis of single points while mass gain by Eq. (7) is averaged throughout the entire sample.

RESULTS AND DISCUSSION

Mass Gain and Strength Development

The specimen temperature increased as soon as the gas was introduced into the chamber. The temperature would typically rise on the order of 25 °C by the time the chamber had reached the desired pressure of 500 kPa; the desired chamber pressure was reached within 60 seconds. The temperature reached a maximum within the first few minutes and gradually declined thereafter.

Table 3.2 summarizes the maximum temperatures reached during the carbonation of both the powder and compact specimens and the water loss during the carbonation of the compact specimens. The carbonation heats of reaction for the main calcium silicate phases are 347 kJ/mol for C_3S and 184 kJ/mol for β-C_2S (Goodbrake et al. 1979a) while 74 kJ/mol is released during carbonation of calcium hydroxide (Moorehead 1986). The highly exothermic nature of the carbonation reaction leads to the release of heat which contributes to the rapid solidification. In each case, the maximum temperature measured in the carbonation of the powdered samples was significantly higher than the temperature rise detected in the compact sample. The greater temperature rise could be a reflection of the higher porosity of the powder providing more sites for reaction which might result in a more vigorous exothermic release.

In the tests on the cement samples the mass of the water recovered from the chamber was on the order of 26% of the amount of mix water used in the compact specimens. There were no hydrate phases detected in the as-received cements which implied that the water collected from the carbonation of these samples was attributable to water being expelled or evaporated from the samples due to the reaction. Water is an essential part of the carbonation reaction and water starvation has been understood to be a possible limiting factor in the reaction (Young et al. 1974) and, thus, the uptake. It has been proposed that for low w/c compacts the evaporation of water caused by carbonation can limit the potential reaction to approximately 25% of the maximum (Berger et al. 1972). While the referenced work used a slightly different mix design, a mixture of C_3S and β-C_2S with 0.125 w/s, it was indicative of the effect that water starvation might have on total uptake. Significant water loss was observed in lime compacts. Since the carbonation of $Ca(OH)_2$ produces water, the measured water loss would include both original mix water and water released from $Ca(OH)_2$ due to carbonation.

Figure 3.2 shows the carbonation data for the materials in the as-received, carbonated powder and carbonated compact conditions. The two cements had a final CO_2 content, as measured by infrared, of about 12% for the Type 10 and over 14% for the Type 30. The carbonated EAF slag samples attained about 13% CO_2. The GGBF slag had the least uptake with only about 7%. Both fly ash and lime showed a significant carbon content in their as-received forms. It was verified by their high percentage of loss on ignition (LOI) in XRF tests (Table 3.1). The high carbon content in as-received fly ash and lime was likely due to the free carbon in fly ash and, as detected through XRD analysis, uncalcined calcium carbonates. To determine the net CO_2 uptake by the two materials through carbonation-curing, the initial carbon was subtracted from the carbonated fly ash and lime samples. Table 3.3 summarizes the net increase of CO_2, the estimate of the carbonation capacity as predicted by the Steinour formula (Eq. 4) and the carbonation degree defined by Eq. (6). The calculations suggested that over 25% of the CO_2 reactive materials reacted in the two cements and the EAF slag while the GGBF slag had a carbonation degree of only about 15%. Significantly higher reaction was seen in the fly ash and lime tests with over 45% and 72%, respectively, of the reactive materials reacted. The results in

Table 3.3 do not represent a maximum achievable carbonation degree for these materials. The carbonation of a given material will be optimum at a specific w/s (Johnson 2000) and compaction pressure for that w/s (Sorochkin et al. 1975) and the present test conditions did not necessarily find the ideal conditions for each material.

When comparing the carbonation results reported in Table 3.3 to the temperature rise in terms of the sample form, it is seen that, although the carbonation consistently produced higher maximum temperatures for materials in the powder form, the final CO_2 contents as measured by infrared do not show any consistent difference in the level of carbonation. Thus the reduced porosity of the compacted sample did not have an adverse effect on the overall carbon uptake.

The difference in the temperature rise between the carbonated Type 30 powder (131 °C) and the Type 10 powder (116 °C) may be attributed to the difference in the fineness of the two cements. The smaller particle size for the Type 30 cement would provide a greater surface area on a mass basis which would translate into a greater number of initial sites available for reaction with the CO_2 before carbonation limiting factors act. It has been previously demonstrated (Goodbrake et al. 1979a) that the degree of carbonation of C_3S and β-C_2S powder increased with increased particle surface area. The presented results show that the Type 30 cement powder had a higher net CO_2 uptake than the Type 10 powder. Conversely, when making a comparison between the carbonation of the compact cement specimens, only a small difference was observed in terms of the maximum temperature achieved, the net percent CO_2 increase and the degree of carbonation. The advantage displayed by the increased fineness of the Type 30 cement seems to have been eliminated when it is carbonated in a compacted form.

The carbonation degree of the two cements and EAF slag was comparable to the estimate of the suggested reaction limit, approximately 25% (Berger et al. 1972), due to water starvation.

Conversely, the higher carbonation degree of the fly ash and lime reflects the fact that the carbonation reaction of the $Ca(OH)_2$ in these specimens produced water and thus reduced or eliminated the reaction limiting effects associated with water starvation. It is clear that $Ca(OH)_2$ is more readily reactive with CO_2 than calcium silicate compounds.

The direct mass gain defined by Eq. (7) for the carbonated compacts is compared to the net CO_2 content as measured by infrared analysis of the powder collected from the same sample in Figure 3.3. The point based CO_2 content was observed to differ from the average-based mass gain by only a few percentage points in all cases except for the lime.

Table 3.4 summarizes the results of the strength testing. It can be seen that the strength achieved by the cement samples that were carbonated two hours exceeded the strength of comparable specimens allowed to hydrate for 7 days. This rapid strength development is consistent with established work (Young et al. 1974). The strengths developed by the GGBF slag, EAF slag and the fly ash were not high enough to be considered for use as structural materials. However, these materials can be used as supplementary cementitious materials in concrete products to assist CO_2 uptake during carbonation-curing and promote secondary cementitious reactions in the subsequent hydration. Lime had also developed sufficient strength within two hours of carbonation and could be combined with other materials to make special building products through a carbonation-curing approach.

XRD Analysis

XRD analysis was performed to confirm the products of carbonation and to identify what phases were consumed in the reaction. Evidence suggested that $Ca(OH)_2$, $3CaO \cdot SiO_2$ and $2CaO \cdot SiO_2$ were consumed, but not completely depleted, while calcite was the primary product.

XRD patterns in Figure 3.4 showed evidence of some pre-existing carbonates (present as calcite) in the as-received lime while the carbonated lime sample pattern included some weak $Ca(OH)_2$ peaks which indicated that not all of the carbonatable material reacted. There was a good match when comparing the XRD pattern of the carbonated lime to the XRD pattern of natural calcite which confirmed that the major carbonation product was calcite. There was also some formation of the aragonite (orthorhombic) polymorph of calcium carbonate. Aragonite has been suggested to form when the system is allowed to dry out (Goodbrake et al. 1979b) which may have been a factor in these tests given that the water collected in the chamber after the test nearly exceeded the amount of mix water included in the specimen.

The XRD patterns of as-received, carbonated and hydrated Type 10 cement are compared and shown in Figure 3.5. The carbonated samples showed new XRD peaks corresponding to calcite while the hydrated specimens showed the formation of calcium hydroxide. Both of these samples showed a reduction in intensity of the peaks associated with C_3S and C_2S in the carbonated specimens. A rough, semiquantitative assessment can be made about the consumption of C_3S by carbonation and hydration through a comparison of the intensities of strong C_3S peaks at $2\theta=34.3°$, 41.2° and 51.7° as they varied between the three trials. Peaks at these locations were free from overlap by strong peaks from other identified compounds. An additional consideration of the peak at 32.1° is also of value since this location shows strong peaks for both C_3S and C_2S. A summary of these peak intensity comparisons can be seen in Table 3.5 and suggested that significant consumption of C_3S and C_2S has occurred in both the carbonated and hydrated samples. However, the continued presence of non-carbonated phases in the carbonated sample, as indicated by strong calcium silicate peaks, suggests that carbonation was not completed and supports the observation that CO_2 uptake was significantly lower than the theoretical capacity of the materials. The XRD patterns and analyses of the Type 30 cement resembled the patterns and analyses of the Type 10 cement.

The XRD analyses of GGBF slag confirmed that the microstructure of the as-received material was glassy (Figure 3.6). The main carbonation product was identified as aragonite but due to the nature of the XRD pattern it was not possible to associate the formation of carbonation products with the depletion of any specific phases. This material had the highest MgO content but there was no indisputable evidence of either crystalline MgO containing phases in the as-received XRD pattern or a carbonated Mg bearing phase in the carbonated GGBF slag XRD pattern. The fact that the GGBF slag sample showed the lowest degree of reaction suggests that the material was relatively unreactive in contrast to the chemisty-based carbonation capacity predicted by the Steinour formula.

The XRD of EAF slag in Figure 3.7 suggests that, in addition to the major carbonation product of calcite, there were traces of aragonite and vaterite (the hexagonal polymorph of calcium carbonate). The major XRD peak differences are summarised in Table 3.6 and show that strong β-C_2S XRD peaks decreased in intensity in the carbonated sample.

The XRD of fly ash in Figure 3.8 shows that significant amounts of $Ca(OH)_2$ were present in the as-received condition. The only compounds identified in XRD of the as-received material were $Ca(OH)_2$ and SiO_2 – no carbonate products were identified despite the significantly high CO_2 content as suggested by the infrared measurement. The IR results were thus interpreted to have detected CO_2 produced by the oxidation of carbon rather than carbonate. The main product of carbonation was calcite. There was a small peak around 9° that may suggest traces of woodfordite, a carbonated form of ettringite that has the chemical formula $Ca_6Al_2(SO_4,$

SiO_4, $CO_3)_3(OH)_{12}\cdot 26H_2O$. Comparisons between the scans suggest that it is the calcium hydroxide in the as-received sample that reacted to form calcite in the carbonated sample.

SEM Analysis

Figure 3.9 shows the microstructure of an area near the surface of the carbonated Type 10 cement compact. It can be seen that the particles appear to be covered by irregular, flaky and grainy products with dimensions on the order of 1 μm. The products have fused into a coating that makes it difficult to discern the shape or location of the original cement particles. It has been suggested (Berger et al. 1972) that the carbonation reaction products end up becoming intermixed with C-S-H such that it is impossible to identify distinct carbonation product morphologies by SEM. Nevertheless, it is clear that the gel and the carbonation products have filled the spaces between the particles or even fused them together. In contrast, the microstructure of the hydrated Type 10 specimen as seen in Figure 3.10 displays distinct morphological evidence of $Ca(OH)_2$ plates, ettringite needles and a more open structure. Figure 3.11a shows a SEM photomicrograph taken close to the centre of the carbonated Type 30 compact. Some acicular or flaky products can be seen and were identified as calcite. The EDS of carbonated cement shows that the products are mixture of calcium, oxygen and carbon supporting their identification, by XRD, as calcite (Figure 3.11b). These elements were also detected in all other carbonated compacts. These crystal carbonates may play a role in preventing complete carbonation of the calcium silicates once they have deposited on the surface of agglomerated cement grains and prevent the necessary reactants, carbon dioxide and water, from contacting the un-carbonated core of cement agglomerates.

An SEM image of the carbonated lime compact can be seen in Figure 3.12. The products appear grainy with some stubby laths evident. No $Ca(OH)_2$ crystals are identified which is in agreement with the near total conversion suggested by the XRD data.

An SEM photomicrograph of carbonated GGBF slag can be seen in Figure 3.13. There appear to be irregular flaky products, approximately 1 μm across, sitting atop a GGBF slag particle. The EDS scan of the carbonation product confirmed the flake to be carbonation products. The products appear to be situated loosely over the GGBF slag particles rather than fused with each other or joining the particles together. This non-fused arrangement is in accordance with the low CO_2 uptake and strength development.

The SEM micrograph of the carbonated EAF slag, shown in Figure 3.14, shows that the individual original particles are not discernable. The carbonation products appear somewhat fibrous while the appearance of a highly fused structure supports the observation of a strength higher than was found for the fly ash or GGBF samples. The EDS indicated the presence of calcium, carbon and oxygen suggesting the formation of a carbonation product.

The carbonated fly ash, as shown in the SEM photomicrograph in Figure 3.15, did not develop a fused microstructure. An individual fly ash particle can be easily identified and appears to be largely unreacted. The carbonation products appear to be flaky and dispersed. Some particles have been fused together but the microstructure appears porous which may explain the low strength observed. The chemical composition and the Steinour carbonation capacity estimate suggested that there was only about half as much carbonatable material in the fly ash as was present in the other materials.

CONCLUSIONS

The CO_2 uptake of six cementitious materials (Type 10 cement, Type 30 cement, GGBF slag, EAF slag, fly ash and lime) was significantly less than their theoretical maximum. The two cements and the EAF slag each had a CO_2 uptake of slightly over 12% which was well below the capacity of about 50%. The lime and fly ash showed the highest degree of carbonation and the GGBF slag the lowest. Evidence suggests that the carbonation reaction may have been limited due to water starvation. The cements, in particular, lost more than 25% of the mix water due to vaporisation caused by the exothermic heat rise associated with the carbonation. The water loss was about 20% in the slags, 10% in the fly ash and 90% in the lime. The primary product of carbonation was calcite except for the carbonation of GGBF slag which favoured aragonite. The phases consumed were C_2S, C_3S and $Ca(OH)_2$.

A comparison between the two cements suggested that an increase in fineness provided an increase in the carbonation of the powder samples but showed no significant difference between the carbonation of the two compacts. The large surface area in finely ground cement could not be taken advantage of if the cement is densely packed. The carbonation capacity of compacted samples was comparable to that of the powdered samples, indicating that porosity of the compacted samples was not a critical limiting factor for CO_2 uptake. The temperature rise was higher for the powdered samples which may have been related to the more porous arrangement of material allowing for a more vigorous reaction. However the CO_2 uptake was not seen to be higher in powdered samples. The carbonation reaction could have been slowed considerably when the powder agglomerates became coated by carbonation products and when the water starvation started to occur.

On the basis of CO_2 uptake both EAF slag and fly ash would make a suitable cement replacement. The EAF slag has the additional benefit of high early strength gain. The fly ash had a high $Ca(OH)_2$ content which was shown to counteract water starvation and permit a greater degree of reaction. This aspect would be a promising factor for designing a blended cement to promote maximum carbon dioxide uptake and strength gain. The use of industrial wastes, such as slag and fly ash, promotes more net gain in global CO_2 sequestration activities.

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TABLES

Table 3.1: Chemical Compositions of Materials

	Type 10 cement	Type 30 cement	GGBF slag	EAF slag	Fly ash	Lime
CaO	63.1	62.9	38.5	36.5	29.6	61.4
SiO_2	19.8	19.6	40.1	12.9	27.6	1.1
Al_2O_3	4.9	4.9	7.8	5.9	14.6	0.5
Fe_2O_3	2	2	0.74	24.9	2	0.2
MgO	2	2	9.7	9.5	0.55	0.7
Na_2O	0.85[a]	0.89[a]	0.38	0.08	0.21	0.03
K_2O	-	-	0.53	0	1.19	0.01
SO_3	3.8	4	2.21	0.28	0.35	0.02
LOI	2.8	3	0.22	2.8	23.4	34.9

a - Na_2O alkali equivalent including K_2O

Table 3.2: Peak Temperature and Water Loss of Carbonation

Material	Peak Temperature (°C)		% water lost from compacts[a]
	Powder	Compact	
Type 10 cement	116.0	70.0	26.3
Type 30 cement	131.0	68.0	26.7
GGBF slag	83.1	41.5	19.3
EAF slag	106.8	45.2	21.1
Fly ash	131.7	70.1	10.8
Lime	117.0	60.0	92.4

a – expressed as a percentage of original mix water

Table 3.3: Net CO_2 Uptake and Carbonation Degree as Determined by Infrared Analysis

Material	Net CO_2 increase (%)		% CO_2 capacity (Eq 4)	Carbonation degree (%)	
	carbonated powder	carbonated compact		carbonated powder	carbonated compact
Type 10 cement	10.9	12.5	50	22.1	25.4
Type 30 cement	12.3	12.7	49	25.9	26.8
GGBF slag	7.9	6.2	41	19.7	15.5
EAF slag	12.8	10.7	39	33.9	28.3
Fly ash	12.9	11.3	25	51.5	45.1
Lime	18.5	23.8	49	56.2	72.3

Table 3.4: Strength of Carbonated Cementitious Compacts

Material	Condition	Thickness (mm)	Age	MOR (MPa)	f_c' (MPa)
Type 10 cement	hydrated	14.3	7 d	4.0	39.7
Type 10 cement	carbonated	14.3	2 h	8.8	56.8
Type 30 cement	hydrated	14.5	7 d	4.3	41.3
Type 30 cement	carbonated	14.3	2 h	9.6	56
GGBF slag	carbonated	16.3	2 h	2	8.7
EAF slag	carbonated	13.3	2 h	4.4	16.6
Fly ash	carbonated	20.5	2 h	1.3	3.5
Lime	carbonated	21.4	2 h	3.3	24

Table 3.5: Comparison of XRD Patterns of Type 10 cement

Peak Location (°2θ)	Ratio		Interpretation
	$I_{carb}/I_{as\ rec}$	$I_{hyd}/I_{as\ rec}$	
32.1	0.4	0.4	C_3S and C_2S
34.3	0.7	0.6	C_3S
41.2	0.8	0.6	C_3S
51.7	0.9	0.4	C_3S

Table 3.6: Comparison of XRD patterns of EAF slag

Peak location (2θ)	Ratio I_{carb} vs $I_{as\ rec}$	Interpretation[a]
Significant decreasing peaks		
31.9	0.5	β-C_2S (RI=100, 97)
32.4	0.4	β-C_2S (RI=83)
41.0	0.5	β-C_2S (RI=51)
New or increasing peaks		
26.1	14.9	aragonite (RI=100)
27.0	1.9	vaterite (RI=100)
29.2	8.6	calcite (RI=100)
48.4	22.3	calcite (RI=17)

a – RI notes the relative intensity of the peak at that location in the XRD pattern of the specified material

FIGURES

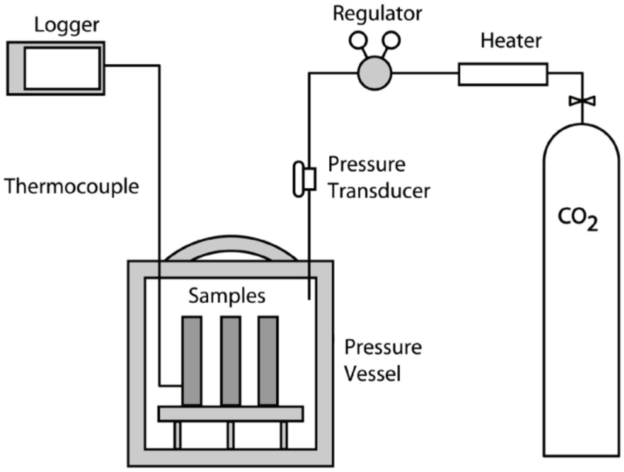

Figure 3.1: Schematic of carbonation setup

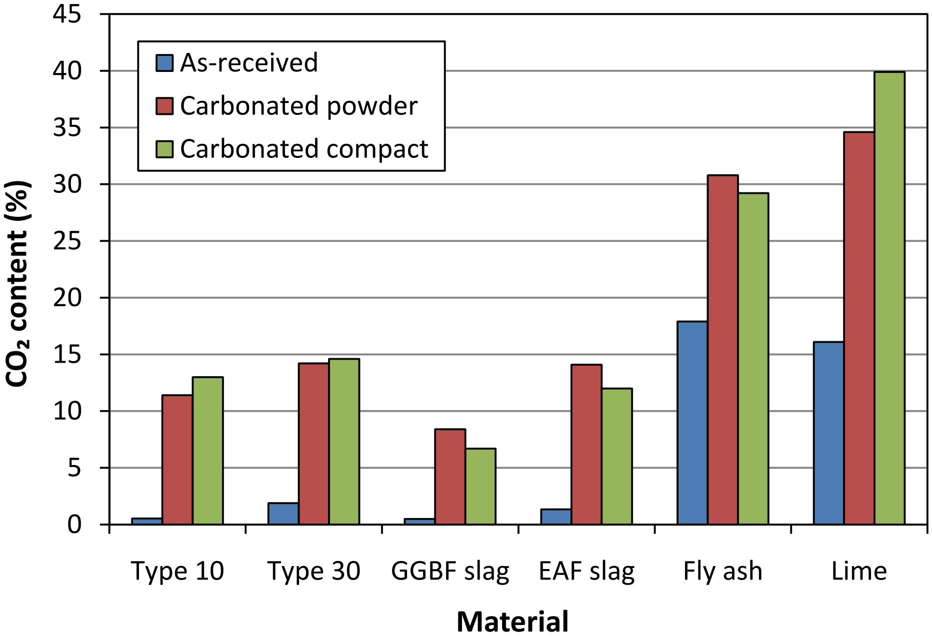

Figure 3.2: Percent CO_2 content of the carbonated samples by infrared analysis

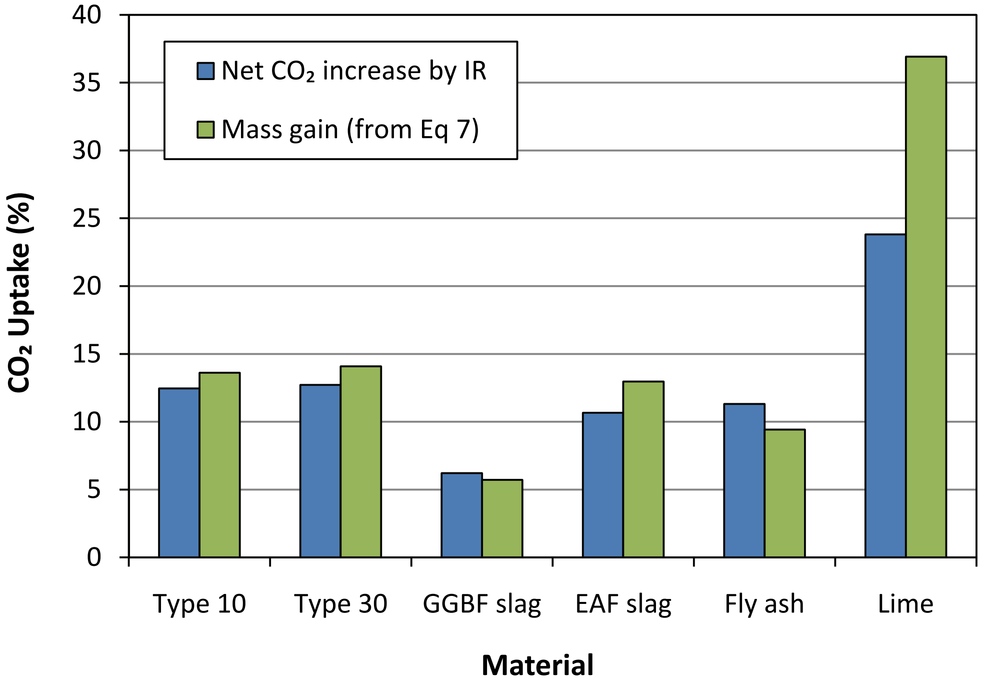

Figure 3.3: Comparison of mass gain to CO_2 content in compact specimens

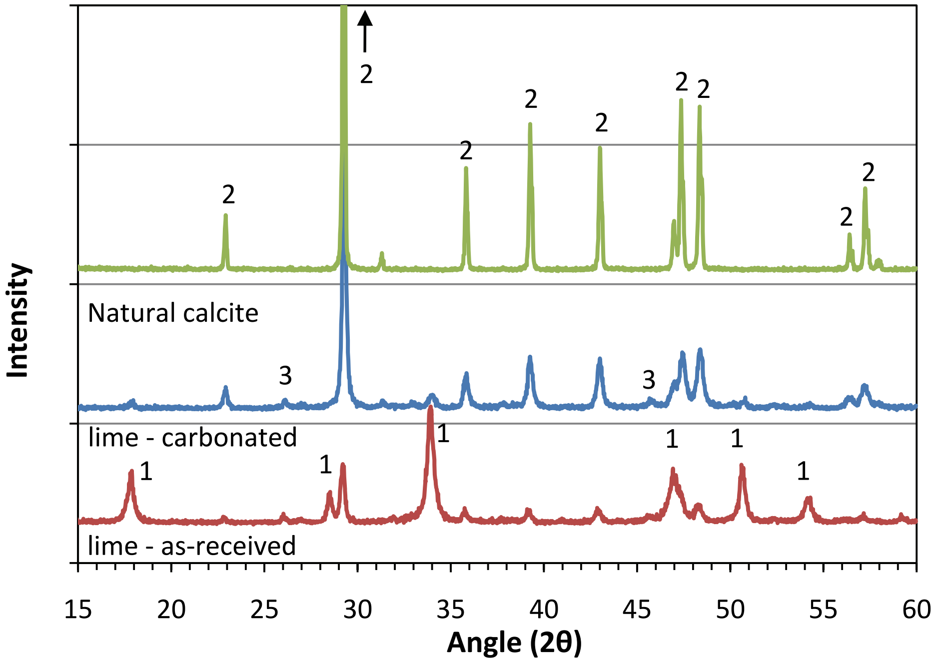

Figure 3.4: XRD Patterns of as-received lime, carbonated lime and natural calcite: (1) calcium hydroxide, (2) calcite, (3) aragonite

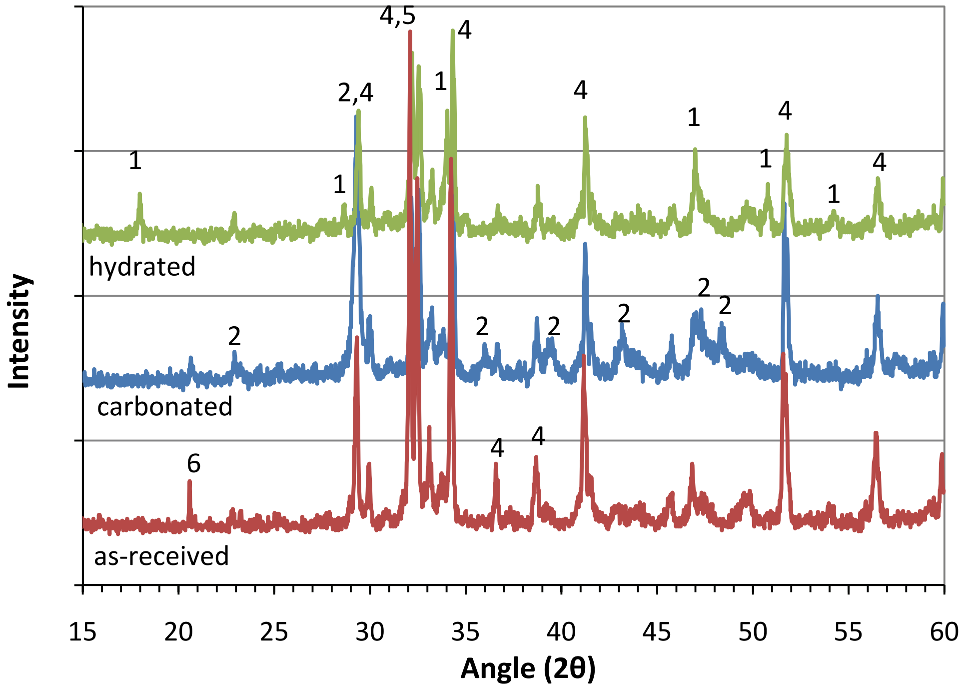

Figure 3.5: XRD Patterns of as-received, carbonated and hydrated Type 10 cement: (1) calcium hydroxide, (2) calcite, (4) C_3S, (5) C_2S, (6) gypsum

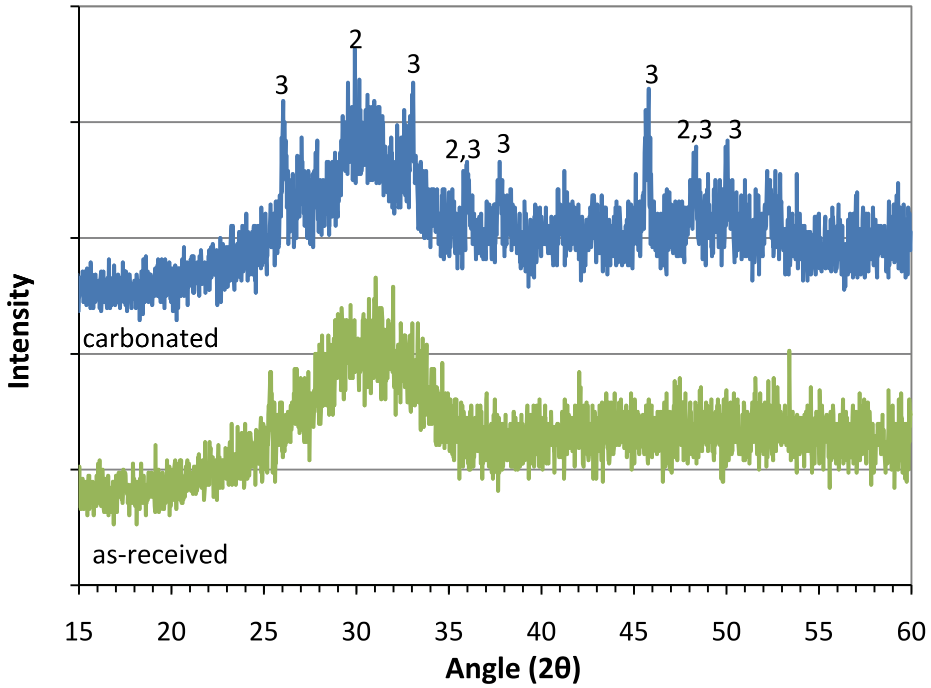

Figure 3.6: XRD Patterns of as-received and carbonated GGBF slag: (2) calcite, (3) aragonite

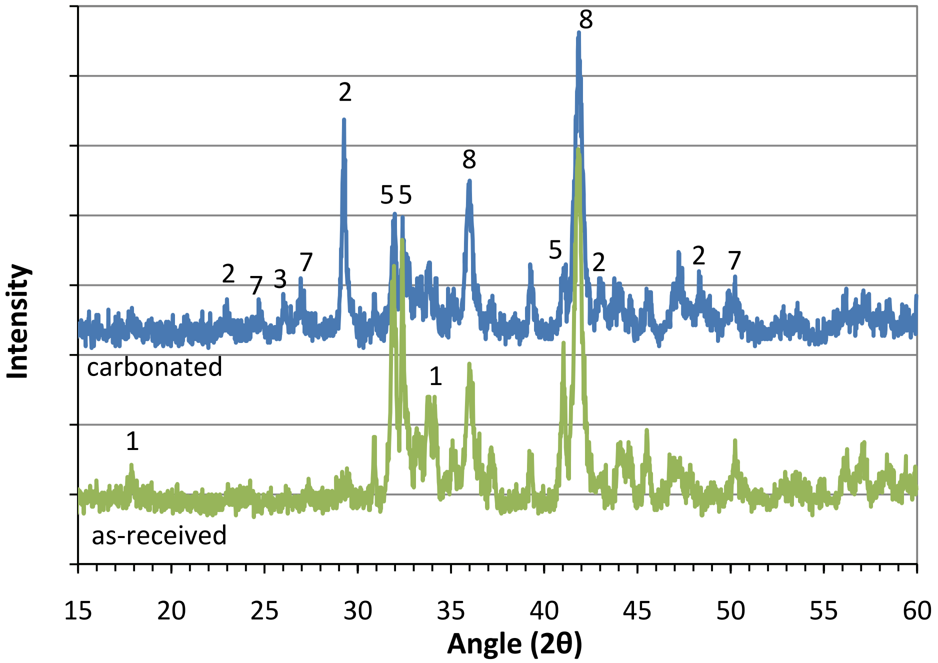

Figure 3.7: XRD Patterns of as-received and carbonated EAF slag: (1) calcium hydroxide, (2) calcite, (3) aragonite, (5) C_2S, (7) vaterite, (8) FeO

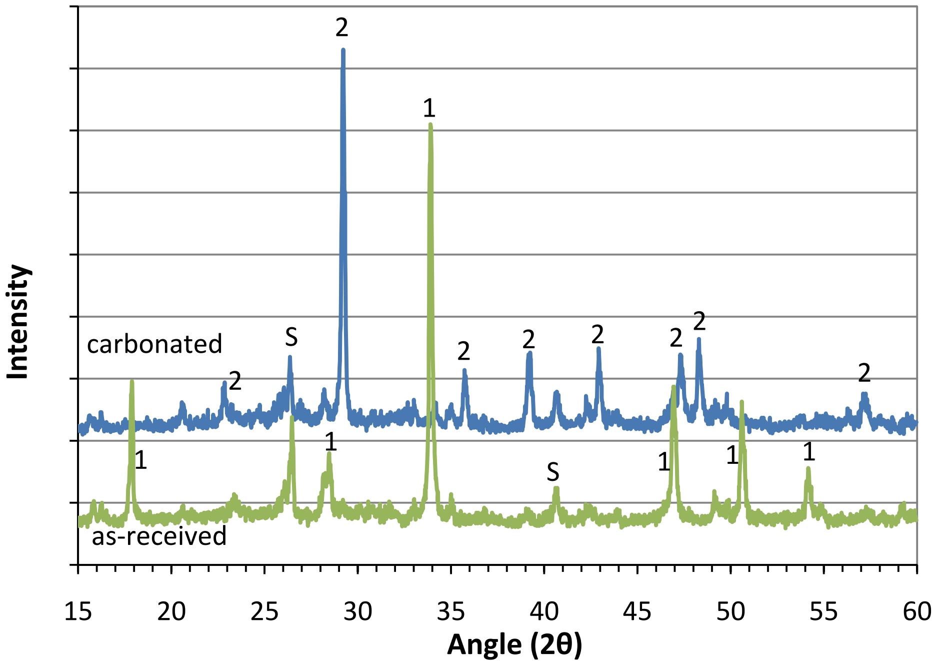

Figure 3.8: XRD Patterns of as-received and carbonated fly ash: (1) calcium hydroxide, (2) calcite, (S) SiO_2

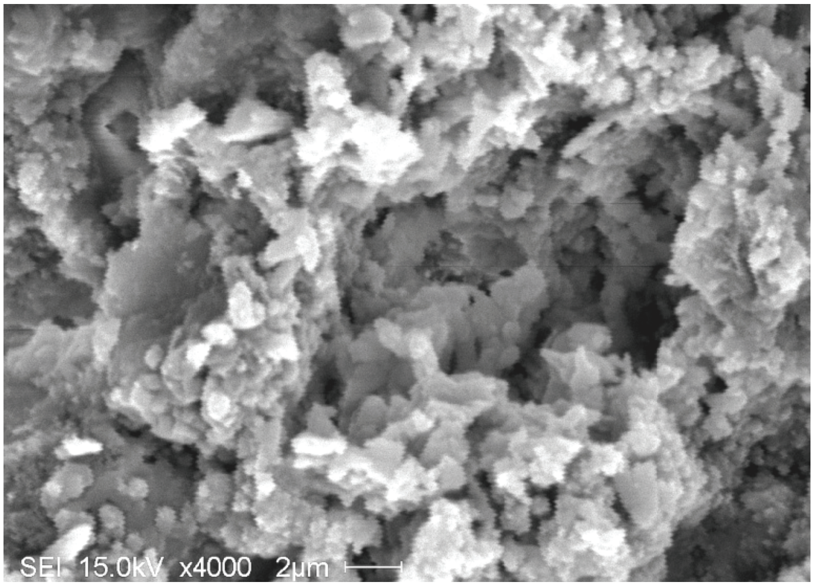

Figure 3.9: SEM photomicrograph of carbonation-cured Type 10 cement compact

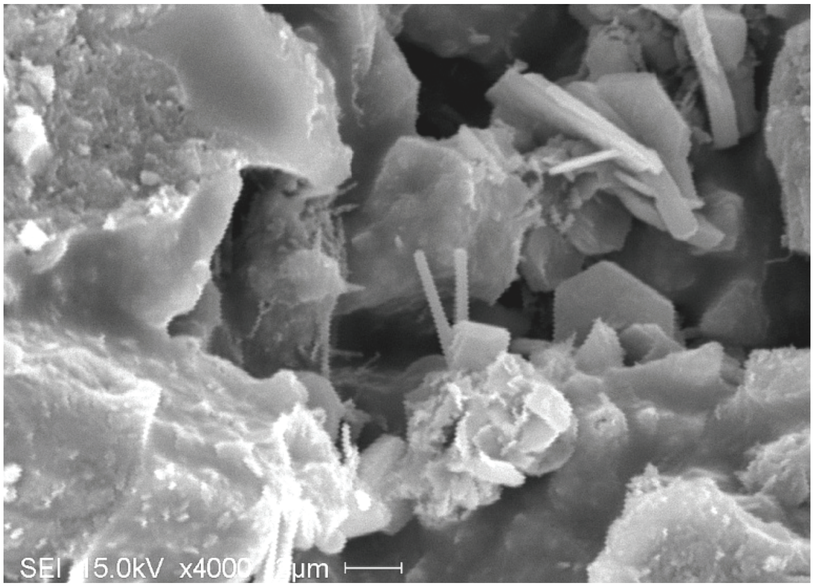

Figure 3.10: SEM photomicrograph of hydrated Type 10 cement compact

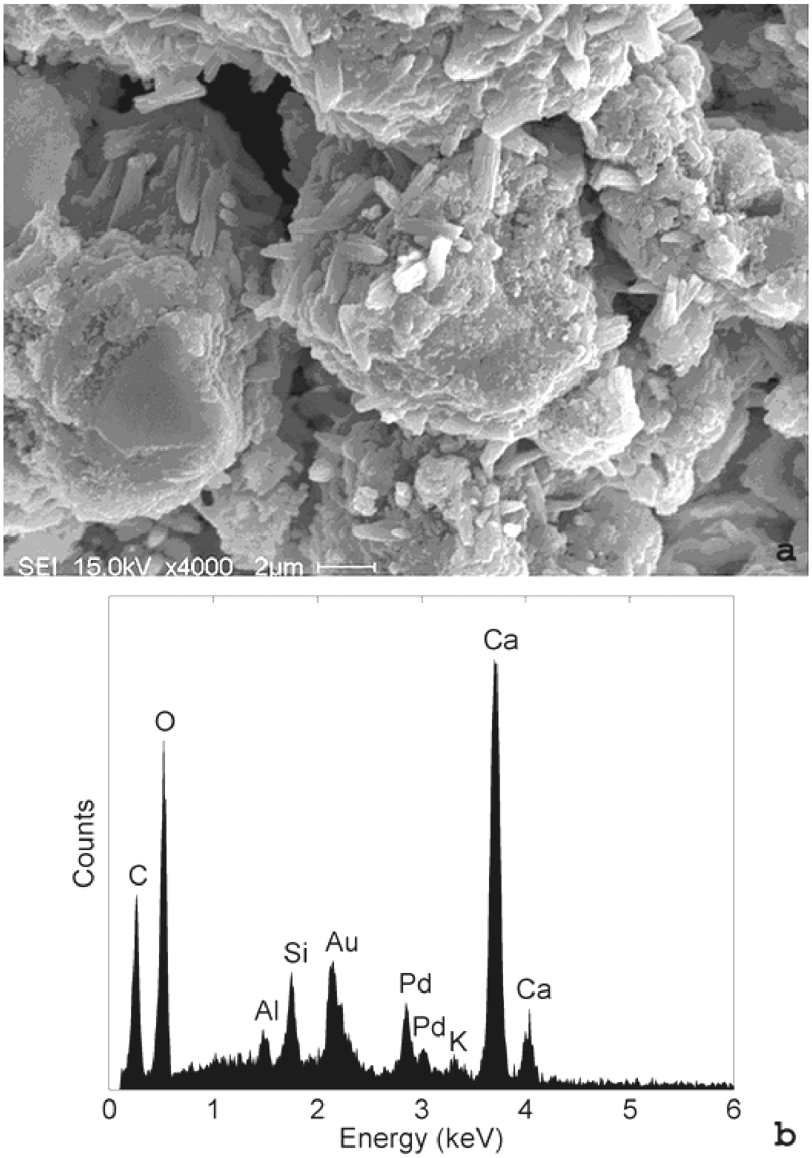

Figure 3.11: Carbonation-cured Type 30 cement compact (a) SEM photomicrograph, (b) EDS of carbonation product

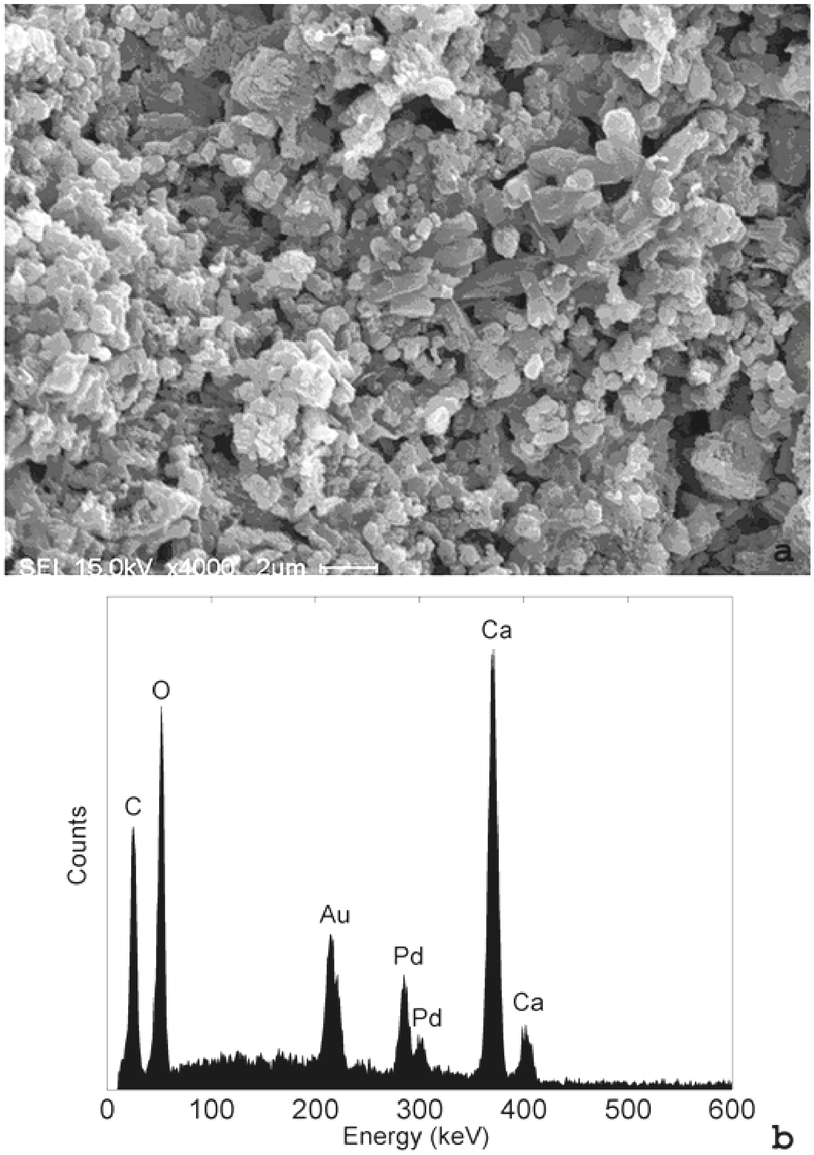

Figure 3.12: Carbonated lime compact, (a) SEM photomicrograph, (b) EDS of carbonation product

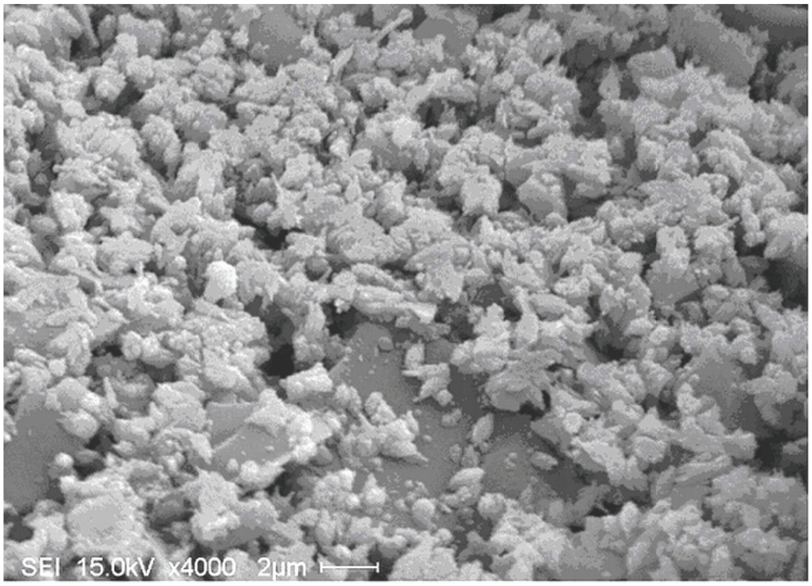

Figure 3.13: SEM photomicrograph of carbonated GGBF slag compact

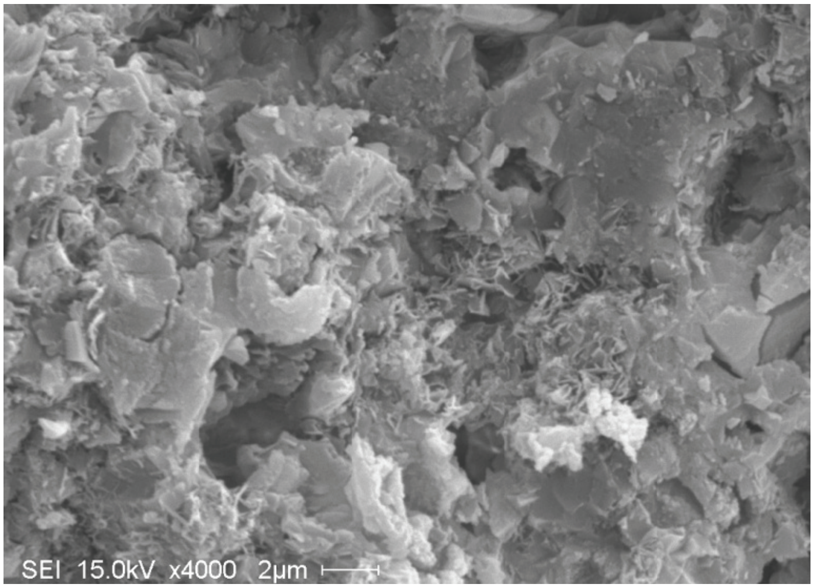

Figure 3.14: SEM Photomicrograph of carbonated EAF slag compact

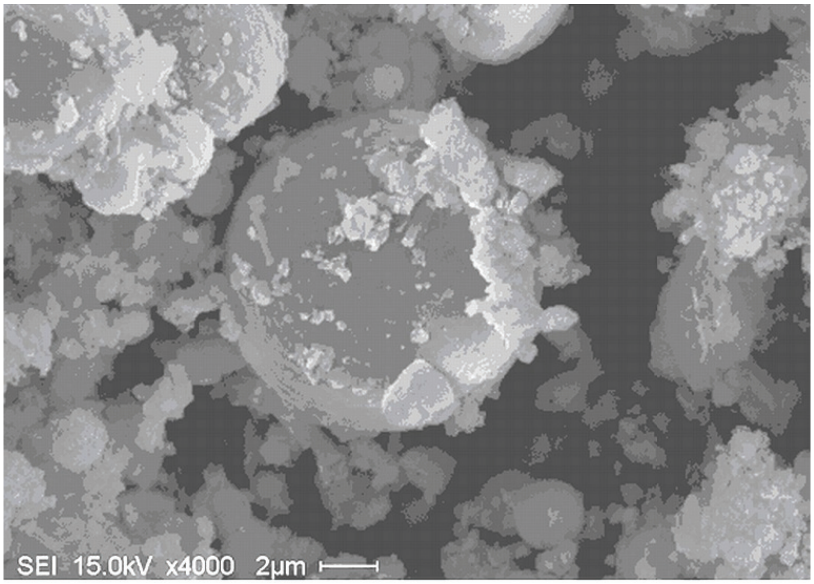

Figure 3.15: SEM photomicrograph of carbonated fly ash compact

Chapter 4

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CARBONATED LADLE SLAG FINES FOR CARBON UPTAKE AND SAND SUBSTITUTE

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Sean Monkman, Yixin Shao and Caijun Shi

PREFACE

The carbonation-curing of cementitious materials proved that a variety of calcium-rich materials had the potential to absorb CO_2 and develop strength in the process. However, the potential is limited by the achievable degree of carbonation ranging from 20% to 30%. This limit is associated with the water used and the density of the products formed. The significant increase in carbon uptake by cementing binders seems difficult without changing concrete forming process. The following chapter explores the possibility of using a sand substitute to increase the total carbon sequestration in concrete. Sand usually accounts for 30-35% of concrete by weight. If some calcium-rich industry waste, such as steel slag, can be carbonated and used to replace sand then the produced concrete will offer the combined benefits of higher CO_2 sequestration and lower consumption of a natural resource. The presented work examined the potential of CO_2 absorption by ladle slag fines with the intention of sequestering CO_2, eliminating free lime, and producing a sand substitute that would serve as a manufactured alternative to natural river sand.

Ladle slag has several characteristics that make it suitable for this phase of the research. While ladle slag is only weakly hydraulic and consequently not traditionally used as cementitious binder, the chemistry of the slag makes it ideal for reaction with carbon dioxide. The as-received slag has a fine grading curve that gives it a particle distribution comparable to sand without the need for additional processing or crushing. However, the as-received slag is not employed as a fine aggregate because of a high free lime content and attendant volume stability issues in service. The carbonation treatment had potential to both absorb CO_2 and eliminate the problematic free lime. The investigation of use of a waste material, ladle slag, in concrete extends the employment of industrial wastes (traditionally, blast furnace slag, fly ash, and silica fume) in concrete materials.

The research considered two different approaches for carbonation. The high pressure carbonation requires a pressure vessel which is specialized equipment that might act as a barrier to subsequent extension to industrial practice. The alternate method considered atmospheric carbonation of slag and represents a relatively simple approach with lower equipment demands and lower energy requirements.

The work is presented in the form in which it was accepted for publication by the ASCE Journal of Materials in Civil Engineering.

ABSTRACT

The possibility of using a carbonated ladle slag as a fine aggregate in concrete was investigated. The slag was treated with carbon dioxide to reduce the free lime content while binding gaseous CO_2 into solid carbonates. The treatment took place with either a high concentration of CO_2 at 500 kPa for 2 hours or with a low concentration of CO_2 at atmospheric pressure for 56 days. It was found that CO_2 uptake by the slag particles between 300 and 600 μm and by the slag particles smaller than 75 μm was about 4.2% and 15.6% of their mass respectively. The extractable CaO contents were estimated by titration and were found to be significantly reduced by carbonation treatment. The carbonated ladle slag was used as a fine aggregate in zero-slump press-formed compact mortar samples and compared to similar samples containing a control river sand. The 28 day strengths of the mortars made with the carbonated slag sand were comparable to the strengths of the normal river sand mortars. The use of carbonated ladle slag as a fine aggregate in concrete is shown to be a novel way of sequestering CO_2 in a beneficial manner.

INTRODUCTION

In many areas there is a current, or developing, need to use replacements for natural sands in concrete to reduce energy consumption through transportation or preserve natural resources (Stewart et al. 2006). Many industrial waste materials can potentially to be used as economic and environmentally-friendly sand substitutes for cementitious building products (Ramachandran 1981). Examples include fine aggregates produced from granulated blast furnace slag (Yüksel et al. 2006), copper slag and fly ash (Ishimaru et al. 2005), and quarry residue fines (Malhotra and Carette 1985).

Ladle slag is a calcium-rich by-product from the steel refining process. Traditionally, it is considered to be unsuitable for use as a cementitious material because it typically contains a high level of free CaO and has poor hydraulic properties (Shi 2002; Shi 2004). Although unsoundness of the ladle slag limits its use as aggregates, in a concrete product or as a road base material, it has been examined as a useful lime-bearing addition to masonry mortar and as part of a soil-cement mixture used for road paving (Manso et al. 2005). Common practice dictates that steel slags intended for use as a construction material (either as aggregates or as road base materials) should be weathered for an extended period to reduce the amount of free CaO and its associated hydration expansion in service (Juckes 2003). The advantage of using ladle slag is that the finely graded powder can approximate the grading of a natural sand without additional crushing requirement. The high CaO content of the slag makes it an ideal material to capture carbon dioxide and convert it to thermodynamically stable calcium carbonates.

Carbon dioxide sequestration is considered as one of several important components in the global greenhouse gas reduction strategy. The direct capture of anthropogenic CO_2 from industry point sources for permanent storage in geologic formations and depleted oil reservoirs, deep into the oceans, or in magnesium silicate minerals have all been investigated (IPCC 2005). Calcium-rich materials also have demonstrated the ability to capture CO_2 by a carbonation reaction to form stable calcium carbonate solids (Johnson 2000; Monkman and Shao 2006). The reaction takes place with deliberate exposure of calcium-containing materials to high concentrations of carbon dioxide. Such accelerated carbonation of slag essentially serves the same purpose as accelerated weathering to the extent that the process can be integrated into slag sand production. The use of carbonated ladle slag as a fine aggregate in concrete would offer several benefits: a) a beneficial use for a globally available metallurgical waste material would divert the ladle slag from landfills, b) a ladle slag made suitable for construction use via reaction with carbon dioxide would offer an economic approach to sequester carbon dioxide thereby helping to mitigate CO_2 emitted from industrial processes such as steel or cement production, and c) developing ladle slag into a suitable fine aggregate would create an alternative aggregate source that would reduce the need to transport suitable natural sands, or the energy required to produce manufactured aggregates.

Carbonation of stainless steel slag was studied for solid waste stabilization. It was reported that the amount of leachable metals, such as chromium, could be reduced by carbonation process (Johnson et al. 2003b). Electric arc furnace (EAF) steel slag has previously been considered as a feedstock for carbon dioxide sequestration in dedicated high pressure (10 to 30 bar) and high temperature (> 200 °C) reactors using a finely ground powder (Huijgen et al. 2005). The purpose of this study is three-fold: 1) to use ladle fines as a CO_2 binder in the as-received condition to avoid energy intensive grinding of raw materials in mineral CO_2 sequestration, 2) to investigate the carbonation behaviour of ladle slag at atmospheric, or near-atmospheric, pressures to further reduce the energy required for the process, and 3) to examine the performance of cement mortar containing carbonated ladle slag as a sand substitute.

EXPERIMENTAL WORK

The ladle slag was acquired from QIT-Fer et Titane steel plant, outside Montreal. It was damp and oven dried at 50°C before use. The material had a range of particle sizes with greater than 90% of the material passing a 850 µm sieve. The few coarse pieces were observed to be steel particles, debris, or large solid pieces of slag and were easily removed from the as-received slag and discarded. The remaining slag was graded according to the fine aggregate grading described in ASTM Standard C33. Its particle size distribution is listed in Table 4.1 together with grading curves for the ASTM standard and for the commercial river sand. The as-received ladle slag is much finer than river sand.

The bulk chemical composition of the slag as determined by XRF is presented in Table 4.2. The initial carbon content (C_0) was measured by a carbon analyzer. The chemistry of ladle slag depends upon the batch of steel and is by no means consistent. However, ladle slags typically have a high CaO content (58 to 60%). Their theoretical maximum CO_2 uptake at 100% carbonation degree is about 50% by mass (Steinour 1959), i.e. one ton of slag could sequester about half a ton of CO_2 into calcium carbonate solids if all carbonatable compounds in the material successfully react with CO_2.

The slag was carbonated with two objectives: to eliminate any free CaO present and to bind CO_2 into $CaCO_3$. Two ways of carbonating the material were pursued. The first approach examined an accelerated exposure treatment for a short period of time using gas at 500 kPa pressure. The second approach treated the slag with carbon dioxide at atmospheric pressure but for longer exposure times. A comparison of the two carbonation approaches allows for an assessment of the feasibility of a low gas pressure and thus a low energy process to facilitate CO_2 sequestration and create carbonated slag fines.

For the accelerated exposure process, the slag was carbonated in a sealed chamber, as shown in Figure 4.1. For slag powder of particle size passing 600, 300, 150 and 75 μm, 240 grams of each was mixed with water, with a water to powder ratio ranging from 0.080 to 0.175 in a mechanical mixer. The moistened powder was placed in the chamber which was evacuated to about 50 kPa below atmospheric pressure to remove the air. The chamber was then filled with CO_2 of 99% purity to a pressure of 500 kPa and maintained at the set pressure for 2 hours. The chamber was filled such that the ultimate gas pressure was achieved within 45 to 60 seconds. The gas was considered to be analogous to carbon dioxide recovered from an industrial source such as flue gas. A constant supply of gas ensured that any carbon dioxide that was consumed by reaction with the sample was immediately replaced with fresh gaseous CO_2. A thermocouple was placed into the mass of powder to measure the carbonation reaction temperature. The initial mass and final mass of the powder was also recorded. Any water rejected from the sample during carbonation (due to exothermic reactions) condensed on the interior of the chamber and, at the conclusion of the test, was collected by absorbent paper and quantified as mass of the water lost from the sample. The percent mass gain due to CO_2 uptake can be estimated by:

$$Mass\ gain\ (\%) = \frac{\left(Mass_{final} + Mass_{water\ loss}\right) - Mass_{initial}}{Mass_{dry\ binder}} = \frac{\Delta Mass_{CO_2}}{Mass_{dry\ binder}} \qquad (1)$$

The water was included in this calculation because the carbonation process was treated as a closed system. It was assumed that the only water present at the conclusion of the test had been present in the chamber at the beginning of the test either as mixed water or as chemically combined water in the sample (in a phase such as calcium hydroxide). If the increase in mass during the carbonation was solely due to the incorporation of carbon dioxide into solid products then a measure of the mass gain of the closed system could provide an estimate of CO_2 uptake.

The CO_2 content of the carbonated samples was also quantified using an automated carbon analyser (ELTRA CS-800) with an induction furnace and an infrared detector. About 0.2 gram of sample was heated to 1000 ºC and the released carbon dioxide was measured with an infrared sensor. The instrument was calibrated using cement reference materials and synthetic carbonate standards. The measurement expressed the CO_2 content as the mass of CO_2 released upon heating to 1000 ºC as a percentage of the intial, dry, sample mass.

These data were used to make a comparison with percent mass gain in Eq (1) and to calculate a carbonation degree, D_c, based on C_0, C and C_{max}(=50%), the initial, final and theoretical maximum CO_2 content of the material, respectively (Matsushita et al. 2000):

$$D_c(\%) = \frac{C - C_0}{C_{\max} - C_0} * 100 \tag{2}$$

For the atmospheric pressure process, dried slag powder of 330 g for each grade was portioned into an open container (12 cm by 12 cm square) which was placed into a simulated weathering carbonation chamber (Figure 4.2). A minimum of two containers for each slag grading size were tested. The chamber was flushed with CO_2 to create an environment of 50% CO_2 concentration at atmospheric pressure. The relative humidity of the chamber was controlled at 65% to promote carbonation at the maximum rate. The containers of slag were removed from the chamber periodically, weighed, and the material was stirred to promote the exposure of fresh surfaces. Small samples of slag were taken from one of the containers for each grade before they were replaced into the chamber upon whence the relative humidity was returned to 65% and the chamber was re-flushed with carbon dioxide. The long-term exposure lasted 56 days. The mass gain of the slag fines exposed to atmospheric pressure carbonation was estimated as the mass difference (between the final conditions, when the measurement was taken, and the initial conditions) expressed as a percentage of the initial dry powder mass. As opposed to the accelerated carbonation mass gain calculated by Eq. 1, no water loss correction was included in the atmospheric carbonation mass gain calculation. The water required for the carbonation reactions came from the humid storage environment rather than from quantifiable mix water. It was observed that only a minimal amount (less than 0.1 g per 4 g of powder sample) of adsorbed water was measurable through drying of the slag and thus the mass difference is concluded to be bound CO_2. The CO_2 content was also quantified by infrared carbon analyser for comparison.

The powder was subjected to XRD phase analysis employing a Philips PW1710 Powder Diffractometer (Cu Kα radiation, scan interval 5-60º 2θ, with each step covering 0.02º and taking 0.5 s). Thermogravimetric analysis was performed (TG Setaram Setsys Evolution), with a heating rate of 10 °C/min up to 1000 °C under an argon atmosphere with a gas flow rate of 50 ml/min. Scanning electron microscopy was conducted with a Hitachi S-3000N to examine the microstructure of the carbonated materials.

A hot ethylene glycol titration method (Javellana and Jawed 1982) was selected to provide an estimate of the free CaO content of the slag. The technique was selected because of its speed and simplicity. The extraction occurred at a temperature of 70 °C for a duration of 5 minutes. Since the titration procedure (as with other free CaO analysis methods) can dissolve both free CaO and calcium hydroxide, the test results are discussed in terms of extractable CaO rather than free CaO.

The carbonated ladle slag treated by atmospheric pressure process was assessed for use as a fine aggregate. The water absorption and specific gravity of the carbonated slag fines were determined and compared to those of the river sand. The mechanical performance of carbonated slag fines were evaluated through mortar tests. Mortars were made using CSA Type 10 cement to aggregate ratio of 0.5 and water-to-cement ratio of 0.2 to allow press-forming of a zero slump mixture. The mixture proportions were based on equivalent volumes to achieve the same thickness for both types of mortars and to eliminate a possible sample size effect. These mortar compacts were intended to simulate the applications of precast products, such as masonry units, paving stones and hollow core slabs, which could be treated further by carbonation-curing. From each batch, three compact samples of 76 × 127 × 14 mm were made using a compaction pressure of 8 MPa.

A comparison was made between mortars made with either river sand or slag sand incorporating carbonated ladle fines. The slag sand was designed to have the same grading as the river sand. Since the grading of the as-received slag was finer than that of the river sand, the carbonated slag-sand was a blend which included a small amount of river sand filling in as the coarse particles (Table 4.3). Mortar compacts were treated with three different methods: (1) carbonated for two hours, (2) carbonated for two hours and subsequently cured in a moist environment for 28 days, and (3) subjected only to curing in a moist environment for 28 days. The carbonation of the mortars investigated the idea of further promoting CO_2 sequestration through the carbonation of cement binder and reducing the amount of free CaO and $Ca(OH)_2$ in the final products. The compacts were subjected to a compressive test immediately after the carbonation-curing as well as after 28-day subsequent curing in a moisture chamber.

RESULTS AND DISCUSSION

Characterization of the As-received Ladle Slag

Table 4.1 compares the results of the sieve analysis of the as-received ladle slag fines with those of the river sand and the ASTM C33 standard fine aggregate grading. The portion of the ladle slag used in this study had a very fine grading with more than 80% of the slag passing a 300 µm sieve. This is much finer than both the ASTM standard grading and the grading of the local river sand. The river sand is at the low end of the grading curve but had an acceptable fineness modulus. The fineness modulus of the ladle slag is beyond the lower range for typical fine aggregates. Use of the ladle slag as a fine aggregate requires additional material to serve as the coarser fraction to produce a slag sand blend that conforms to the river sand grading. Coarse graded river sand was used to make up the larger size fractions. The slag sand blend is proportioned in Table 4.3. The blend is comprised of ladle fines for sizes smaller than 600 µm and appropriately graded river sand for larger particle sizes. The largest size fractions of slag were not available in sufficient quantities to allow for the production of enough sand, made purely of slag, to meet the research needs. With 12% coarse river sand added, the slag-sand blend can have the same grading as the reference river sand, and was used in mechanical tests of mortar compacts.

Thermogravimetric (TG) analysis was performed on the slag samples. Typical TGA curves are shown in Figure 4.3. According to an interpretation of the mass loss data (Kneller et al. 1994), the as-received ladle slag (<75 µm) was determined to undergo a mass loss of 8.4% associated with water lost from the dehydroxylation of calcium hydroxide and 1.0% associated with CO_2 lost from calcium carbonate. Conceptually, this means that 26.1% of the total mass is CaO contained within $Ca(OH)_2$ and 1.3% of the total mass is CaO combined as $CaCO_3$.

Alternately, the as-received slag could be understood to include 34.5% $Ca(OH)_2$ and 2.3% $CaCO_3$, by mass.

The as-received slag was analysed using XRD tests, as shown in Figure 4.4. The main crystalline phase was found to be calcium hydroxide. The secondary crystalline phases were observed to include garnet [$Ca_3(Cr_{0.35}Al_{0.65})_2(SiO_4)_3$], hydrogarnet [$Ca_3Al_2(O_4H_4)_3$], and jasmundite [$Ca_{20.68}Mg_{1.32}(SiO_4)_8O_4S_{2.}$]. There was no indication of the existence of the calcium silicate phases C_2S or C_3S. While the XRD pattern did not conclusively indicate the presence of CaO, the ethylene glycol titration indicated that the as-received slag had an extractable CaO content of 6.50%. To support the titration method, the extractable CaO content of the cement used in the study was found to be 0.64%, a value very close to the manufacturer's data. The XRD and TGA evidence suggested that the carbonation of slag could be dominated by the reaction of $Ca(OH)_2$ with carbon dioxide, in the presence of moisture, to form calcium carbonate:

$$Ca(OH)_2 + CO_2 + H_2O \rightarrow CaCO_3 + 2\ H_2O \tag{3}$$

The SEM examination of the slag fines and the river sand revealed that the river sand particles were angular and homogenous with a generally clean and smooth surface texture (Figure 4.5) while the as-received ladle slag was seen to have a porous and uneven surface that was variously fibrous, crystalline or flaky (Figure 4.6). Although the grading curve of slag had been adjusted to match that of the river sand and allowed for a direct comparison under the microscope, there was obviously a greater appearance of very fine particles observed with the ladle slag.

Production of Carbonated Slag Fine Aggregate by Accelerated Carbonation

The accelerated carbonation of as-received slag fines was performed by exposing the slag to carbon dioxide gas of 99% purity at a pressure of 500 kPa for 2 hours. The XRD spectrum of the carbonated slag, shown in Figure 4.4, suggested the formation of calcium carbonate [$CaCO_3$] and spurrite [$Ca_5(SiO_4)_2CO_3$] and the consumption of hydrogarnet and calcium hydroxide. Since the accelerated carbonation approach involved the mixing of slag with water, the optimum water-to-powder ratio (w/p) for carbonation uptake was investigated. When the slag is carbonated for use as a fine aggregate, maximizing the CO_2 uptake is essential both for the total carbon dioxide bound by the slag and neutralization of the free CaO and free $Ca(OH)_2$. The maximum CO_2 uptake of a cementitious material depends upon the water-to-binder ratio (Johnson 2000). As-received, ungraded slag was subjected to accelerated carbonation and the percent mass gain, percent CO_2 content and the corresponding maximum reaction temperatures are tabulated for various w/p in Table 4.4. It was found that the mass gain and CO_2 content increased as the w/p decreased to 0.09. A w/p ratio of 0.10 was selected for use in the accelerated carbonation portion of the aggregate preparation. The corresponding peak reaction temperature was about 138 °C, and was indicative of a vigorous carbonation reaction.

The accelerated carbonation approach was subsequently applied to graded ladle fines to determine the CO_2 uptake for each size. Slag was sorted into finer size intervals than the ASTM grading scheme to allow for further data points to be collected across the size range of the slag. The w/p=0.10 slag powders were subjected to CO_2 at 500 kPa for 2 hours. Figure 4.7 shows that the mass gain and CO_2 content increased with decreasing particle size. Therefore it is suggested that the higher surface to volume ratio of the smaller particles would contribute to a greater degree of reaction since a greater fraction of the particle volume is accessible for reaction.

Furthermore, it was found that the percentage mass gain by Eq. (1) agreed well with the percentage CO_2 content determined by carbon analyzer, although the principles of the two measurements are quite different. The mass gain method is an average of the uptake by a large mass and it is not sensitive to sampling size due to non-uniform carbonation. Furthermore, the accuracy of this method is subject to the accuracy of the water loss correction. On the other hand, the percentage CO_2 determined by the infrared sensor represents carbon dioxide released from the sample. It is not dependent on the residual mass, requires no water correction and appears to be more accurate. The variation of the results could be considerable owing to the small sample mass (0.1 gram). The best estimate of carbon uptake considers both methods together.

A comparison of the specific gravity and water absorption of the slag-sand blend and the river sand is shown in Table 4.5. The slag-sand blend is shown to be porous. The bulk specific gravity of the slag-sand blend was found slightly lower than that of the river sand. The water absorption of the slag sand blend, at 6.3%, is about ten times higher than that of the river sand.

Production of Carbonated Slag Fine Aggregate by Atmospheric Pressure Carbonation

The results of the atmospheric pressure carbonation with longer exposure times are presented in Figure 4.8. Similar to the accelerated carbonation, the slag had exhibited an increase in CO_2 reaction with a decrease in particle size. It can be seen that the mass gain plots show a relatively smooth increase in CO_2 uptake with time whereas the carbon content plot shows some point to point variation, particularly for the two larger particle sizes. This reflects the fact that the mass gain method considers the entire batch as opposed to the point-based infrared method.

For the long-term treatment at atmospheric pressure, when the mass gains are normalized against the ultimate mass gain at 56 days, the reaction vs time relationships were seen to be very similar for all of the particle sizes. The carbonation uptakes exceeded 80% of the reference 56-day value after 7 days of exposure and had reached 95% within 28 days. Table 4.6 compares the slag fines carbonated under the accelerated conditions with the slag fines carbonated at atmospheric pressure. The observed carbonation degrees ranged from 5.3% at the largest particle size to 28.9% at the smallest particle size. The particle size has more influence on the CO_2 uptake than the gas pressure used in the treatment. Although the atmospheric pressure carbonation treatment provided a slightly lower carbonation degree, it was accomplished with a gas of low pressure and of dilute carbon dioxide concentration and thus suggested an economic approach to sequester CO_2 in manufactured slag aggregates with minimum energy consumption and direct use of flue gas.

Reduction of CaO Content in the Ladle Slag Fines by Carbonation

The extractable CaO content of the as-received and carbonated slag is shown in Figure 4.9. For as-received slag, the extractable CaO was found to be different depending upon the particle size. Differences in chemistry between the different particle sizes of slag have been reported by other researchers (Johnson et al. 2003a). The extractable CaO content was over 6% in the as-received smallest fraction, but under 2% for the slag with larger particles sizes. For carbonated slag, the extractable CaO content was found to be around 0.2 to 0.3%, which represents a reduction of up to a 95% in the extractable CaO content as compared to the uncarbonated condition. The fact that the extractable CaO content of the carbonated slag had been reduced to a level below that of the cement would imply that carbonation effectively consumed the free CaO.

Given that the carbonation degree of the carbonated slag suggested an incomplete chemical reaction, it is reasonable to surmise that the carbonation would proceed from the surface of a particle to the uncarbonated core. To examine the possibility of free CaO being present in the core, the carbonated slag in size ranges greater than 75 μm was ground to pass 75 μm and the extraction and titration tests were performed. Figure 4.9 shows a comparison of the extractable CaO contents as measured on either whole slag particles or carbonated slag that had been subsequently ground to pass a 75 μm sieve before extraction. It can be seen that, by grinding the slag particles, extractable CaO inside the particle is exposed. Thus, the carbonation does not completely consume the extractable CaO throughout the particle. However, it remains that the measured extractable CaO of the whole carbonated particles was much lower than that of the ground particles. Furthermore, this difference is measured even though the extraction and titration is an aggressive process. Thus, the extractable CaO analyses suggest that the carbonation of the particles reduces the extractable CaO with particular reductions on the surface of the particle.

The results of thermogravimetric analysis of the slag (size <75 μm) carbonated in an accelerated process and a reference Portland cement are also shown in Figure 4.3. The main mass losses (water from calcium hydroxide between approximately 375 °C and 500 °C and CO_2 from $CaCO_3$ between approximately 500 °C and 800 °C) are determined from the TGA curves. When comparing the composition of the as-received slag and the carbonated slag in terms of their ignited mass, water associated with calcium hydroxide is reduced from 10.0% to 3.3% (a 66% reduction) and the bound carbon dioxide increases 17-fold from 1.2% to 21.9%. The absolute mass loss (dried original sample mass as denominator) measured by the TGA and associated with bound CO_2 is 16.4%. This is close to the value of mass gain (15.6%) and CO_2 content by IR (15.6%) shown in Table 4.6.

Mortar Containing Ladle Slag Fines

To investigate the feasibility of using carbonated ladle fines as a sand substitute, mortar compacts containing either the slag-sand (Table 4.3) or a control river sand were carbonated at a gas pressure of 500 kPa for 2 hours and tested for strength immediately afterwards. The ladle fines used in mortar tests were treated by atmospheric pressure carbonation. Characteristics of the mortars tested are summarized in Table 4.7. The river sand mortar was about 15% heavier than the slag sand mortar. The slag sand mortar did, however, show a higher carbonation mass gain, which was possibly related to the porous slag sand allowing for a better penetration of CO_2 gas into the sample.

Compressive strengths of the mortars are summarized in Figure 4.10. In a comparison between the carbonated mortars containing the two different types of sand, the river sand mortars had an apparent higher strength than the slag sand mortar both after 2 hours carbonation and after 2 hours carbonation followed by 28 days of moist curing. There was essentially no difference observed in the strengths of the two types of mortars that were moist-cured for 28 days. The slag sand mortar that had been cured after carbonation had a significant increase over the strength after 2 hours of carbonation but did not reach the strength of the reference after 28 days of moist curing. The early carbonation-curing did not hinder the subsequent hydration in a moist environment and strength development.

The SEM examination of the mortars revealed obvious differences depending on treatment and aggregate type. The hydrated river sand mortar shown in Figure 4.11, displayed typical hydration products (long needles of ettringite) but had a relatively open and porous microstructure. The SEM analysis of the hydrated slag sand mortar (Figure 4.12) showed flat calcium hydroxide plates, fibrous C-S-H gel and long ettringite needles though the ettringite was not as large as what was noted in the river sand mortar.

In the 2-hour carbonated river sand sample (Figure 4.13), the binder is coated with crystalline carbonation products, and has a fused appearance. The 2-hour carbonated mortar sample that included the slag sand (Figure 4.14) had a highly irregular surface. There were crystalline laths characteristic of carbonate products and the binder appeared to be fused, but overall a greater porosity was observed than in the carbonated river sand mortar. This may have been related to the greater porosity and more irregular surface characteristics of the slag aggregates. The more porous microstructure probably allowed, or played a part in, the 128% strength increase with subsequent moist curing or hydration while the strength of the denser river sand mortar increased by only 74%. The slag-sand mortar that was carbonated for 2 hours and then hydrated appears to contain new hydration products. The presence of hydration phases support the observation that the strength of the carbonated mortar increased with additional hydration during the moist curing but since they appear to be added to, rather than replacing, the carbonated structure, explains why the carbonated slag mortar has shown a lower strength than comparable non-carbonated mortar.

Table 4.8 summarizes the amount of CO_2 that has been combined in each of the mortars tested at 28 days. The mass of CO_2 in the slag aggregates is based upon the amount of aggregate that was actually used in the samples (accounting for the any small material losses or wastage during sample production). The mass of CO_2 absorbed by mortar during 2-hour carbonation is estimated using Eq 1. These amounts reflect the average uptake by the three specimens considered as a whole. It can be seen that, for the given mix design, the amount of CO_2 absorbed by cement binder was slightly higher than the amount of CO_2 incorporated into the slag fines. The carbonated mortar with slag fines could sequester 25% CO_2 with respect to cement used. The advantage of using carbonated slag fines is therefore readily evident from a sequestration potential perspective.

CONCLUSIONS

Carbonation treatment of as-received ladle slag fines and its mortar compact was investigated. The process has shown the potential to reduce the amount of calcium hydroxide and extractable CaO in slag and convert significant amount of gaseous CO_2 to calcium carbonate solid in an energy efficient manner. The degree of carbonation of the slag exposed to carbon dioxide at atmospheric pressure for 56 days was comparable to slag exposed to CO_2 for 2 hours at 500 kPa pressure. A long exposure but low pressure carbonation method can thus offer an easy and effective way to carbonate the slag and sequester carbon dioxide.

Mortars made with slag sand had strengths comparable to mortars made with the normal river sand when subjected to conventional moist curing. In both cases the carbonated mortars showed significant compressive strength after only two hours of carbonation and the strengths of the mortars increased with further moist curing. Mortars with slag sand that were carbonated and subsequently moist-cured were as strong as slag sand mortars subjected to only hydration, but were slightly weaker than their carbonated counterpart with river sand.

The carbonation of ladle slag appears to make it suitable for use as a fine aggregate. Significant amounts of carbon sequestration could be realized in a potentially useful form that further utilises a waste slag material. Carbonated mortars that use ladle slag sand offer the largest gains in terms of carbon dioxide uptake but the use of a ladle slag sand in a conventionally hydrated mortar would readily offer carbon sequestration benefits without any significant impact on the strength of the mortar.

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TABLES

Table 4.1: Sieve analysis of the river sand and the as-received slag

Sieve	Percent Passing		
	ASTM C33	River sand	Slag as-received
9.5 mm (⅜ in)	100	100	100
4.75 mm (No. 4)	95 to 100	100	100
2.36 mm (No. 8)	80 to 100	100	100
1.18 mm (No. 16)	50 to 85	98	100
600 µm (No. 30)	25 to 60	88	96
300 µm (No. 50)	5 to 30	57	82
150 µm (No. 100)	0 to 10	23	55
75 µm (No. 200)	Up to 5	5	30
Fineness Modulus	2.3 to 3.1	2.3	1.4

Table 4.2: Chemical analysis of the ladle slag by XRF

Species	Mass fraction (%)	
	as-received, bulk	as-received, <75µm
CaO	58.09	60.29
Al_2O_3	15.71	11.07
SiO_2	9.52	6.86
MgO	4.83	4.67
TiO_2	1.15	1.11
Fe_2O_3	0.86	0.89
MnO	0.10	0.12
Na_2O	0.04	0.04
K_2O	0.01	0.00
SO_3	1.79	1.57
CO_2	0.3	0.73
LOI	6.67	15.04

Table 4.3: Slag sand blend for mortar compact tests

Retained on	Incremental Fraction	Mass (g)	Type	Mass gain	CO_2 contained (g)
4.75 mm (No. 4)	0.0%	0.0	-	-	
2.36 mm (No. 8)	0.0%	0.0	-	-	
1.18 mm (No. 16)	2.3%	13.0	River sand	-	-
600 µm (No. 30)	10.1%	55.6	River sand	-	-
300 µm (No. 50)	30.8%	169.8	Ladle slag	4.2%	7.1
150 µm (No. 100)	33.8%	186.8	Ladle slag	6.5%	12.1
75 µm (No. 200)	17.8%	98.0	Ladle slag	8.1%	8.0
Pan	5.2%	28.9	Ladle slag	12.7%	3.7
Total	100%	552.0	-	-	30.9

Table 4.4: CO_2 content, mass gain and reaction temperature of ladle slag carbonated at various water to powder (w/p) ratios

w/p	CO_2 content by IR	Mass gain	Peak Temperature (ºC)
0.09	11.1%	10.8%	129.6
0.10	10.7%	10.6%	137.8
0.11	11.0%	10.1%	122.9
0.125	7.6%	8.9%	110.4
0.15	7.6%	7.7%	102.6
0.175	4.9%	5.1%	70.7

Table 4.5: Properties of the river sand and slag sand blend

Property	River sand	Slag sand blend
Bulk specific gravity (g/cm^3)	2.65	2.44
Bulk SSD specific gravity (g/cm^3)	2.67	2.59
Apparent specific gravity (g/cm^3)	2.70	2.89
Water absorption (%)	0.62	6.34

Table 4.6: CO_2 uptake by carbonated slag fines and their carbonation degrees (D_c)

Size	Atmospheric pressure carbonation			Accelerated carbonation		
	Mass gain	CO_2 content	D_C	Mass gain	CO_2 content	D_C
300 – 600 µm	4.2%	3.8%	5.3%	4.4%	4.5%	6.5%
150 – 300 µm	6.5%	6.0%	8.2%	5.1%	5.9%	8.2%
75 – 150 µm	8.1%	7.1%	12.9%	8.9%	8.5%	15.7%
Pan – 75 µm	12.7%	11.9%	21.4%	15.6%	15.6%	28.9%

Table 4.7: Characteristics of river sand and slag sand blend mortars

	River sand mortars			Slag sand blend mortars		
	C	C + H	H	C	C + H	H
Average thickness (mm)	14.6	14.6	14.8	14.7	14.6	14.6
Density (g/cm^3)	2.04	2.06	2.04	1.78	1.81	1.80
Carbonation mass gain* (%)	11.8	12.7	0	13.4	14.4	0

* based upon mass of cement

Note: C = 2 hr carbonation, CH = 2hr carbonation + 28 days hydration; H = 28 days hydration

Table 4.8: Summary of carbon uptake in the mortars as arranged by treatment history

Property	Using River Sand		Using slag sand blend	
	H	C	H	C
Mass, original total (g)	876.9	876.8	768.9	771.4
Mass, cement binder (g)	274.1	274.1	240.3	241.1
Mass CO_2 in aggregate (g)	0	0	23.3	23.4
Mass CO_2 in cement (g)	0	34.9	0	34.8
Total mass of CO_2 associated (g)	0	34.9	23.3	58.2
% CO_2, by original total mass	0%	4.0%	3.0%	7.5%
% CO_2, by cement binder mass	0%	12.7%	9.7%	24.1%

Note: C = 2 hr carbonation, H = 28 days hydration

FIGURES

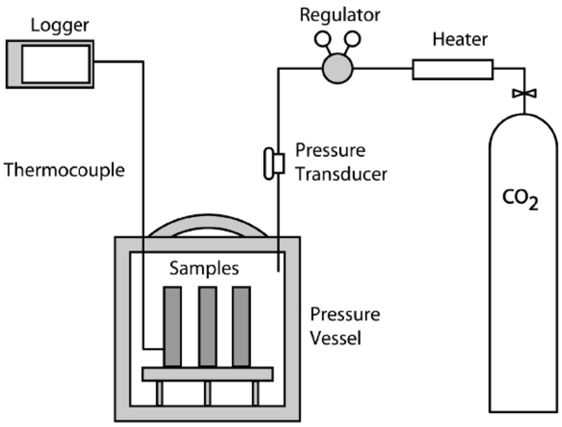

Figure 4.1: Accelerated carbonation setup

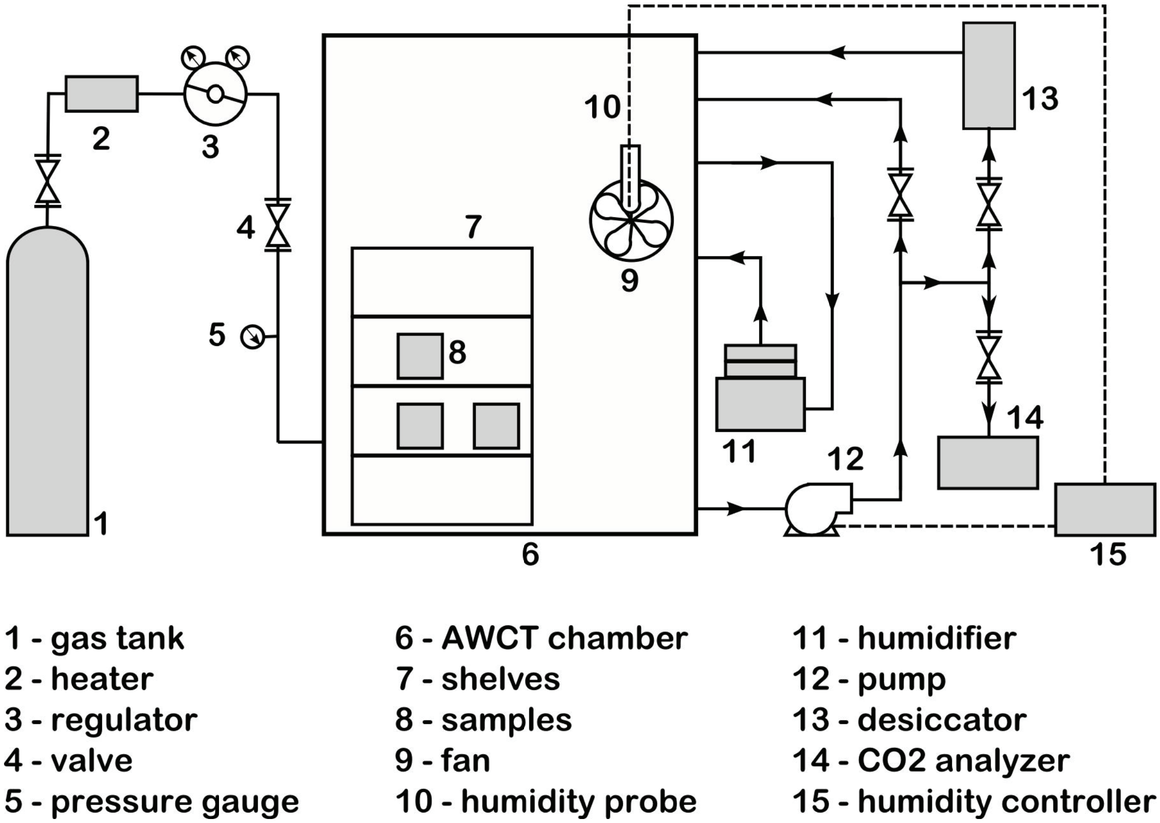

Figure 4.2: Atmospheric pressure carbonation setup

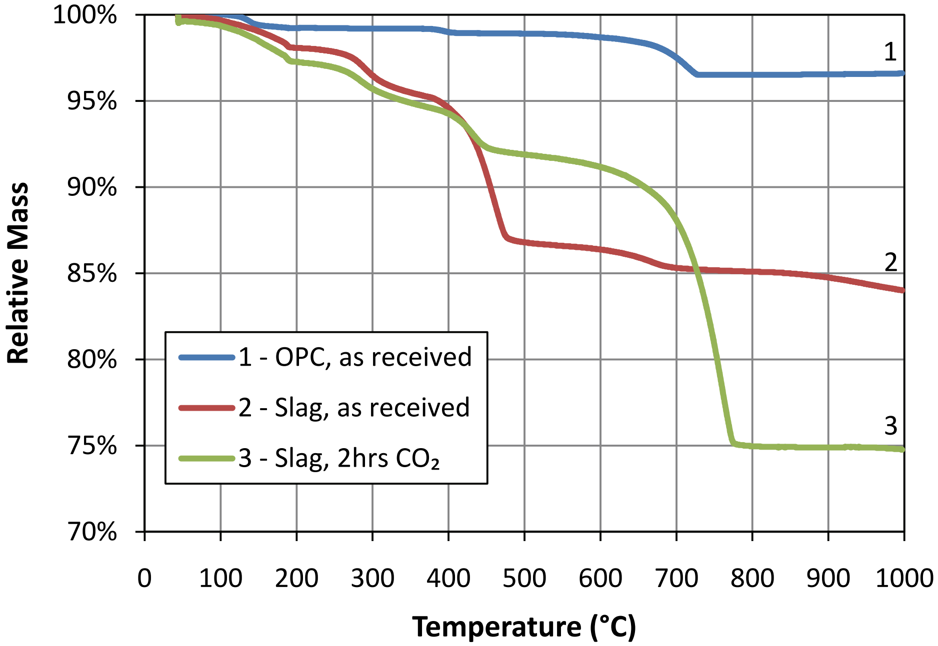

Figure 4.3: TGA curves of OPC, as-received slag and carbonated slag

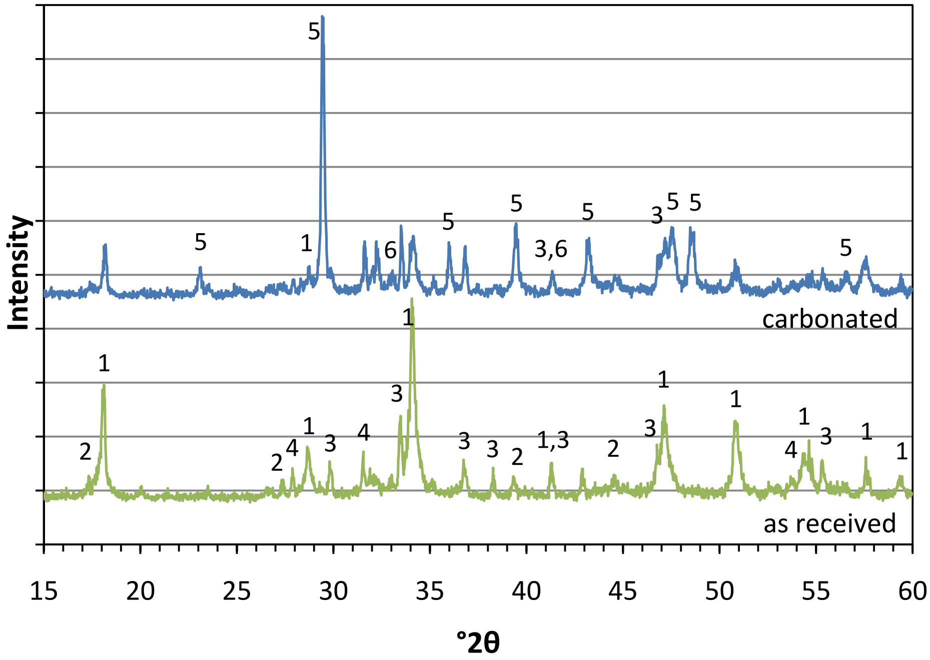

Figure 4.4: XRD of ladle slag before and after carbonation identifying peaks for (1) calcium hydroxide, (2) hydrogarnet, (3) garnet, (4) jasmundite, (5) calcium carbonate, and (6) spurrite

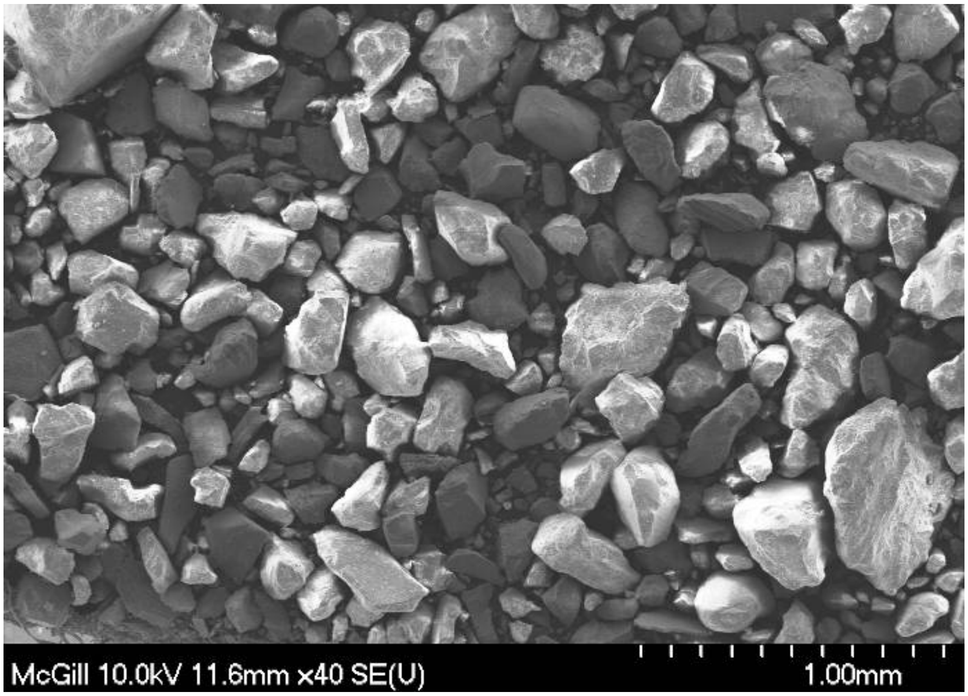

Figure 4.5: SEM image of river sand <600 µm

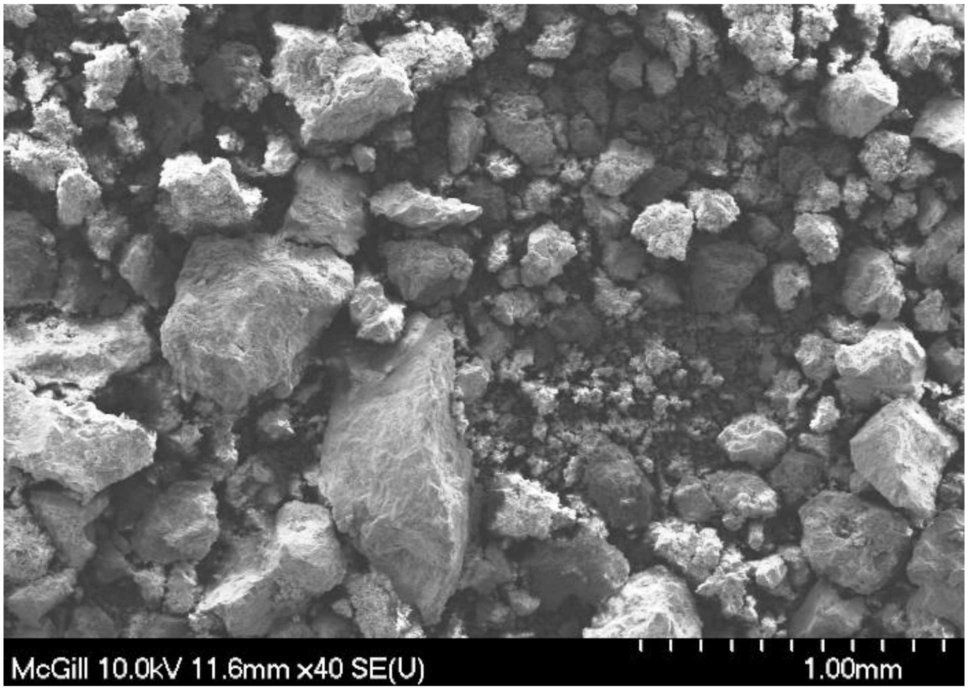

Figure 4.6: SEM image of slag sand blend <600 µm

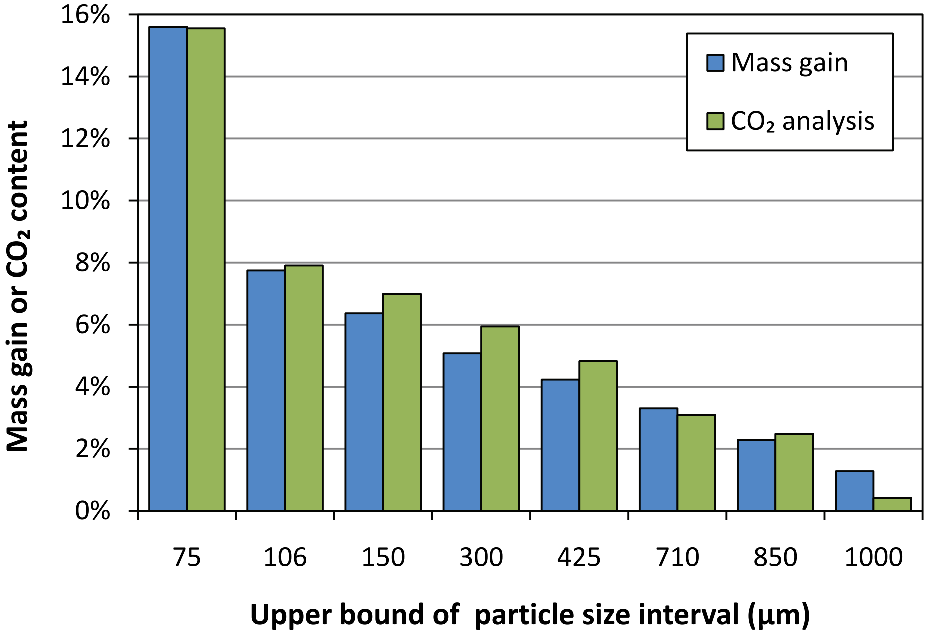

Figure 4.7: Effect of particle size on CO_2 uptake in accelerated carbonation

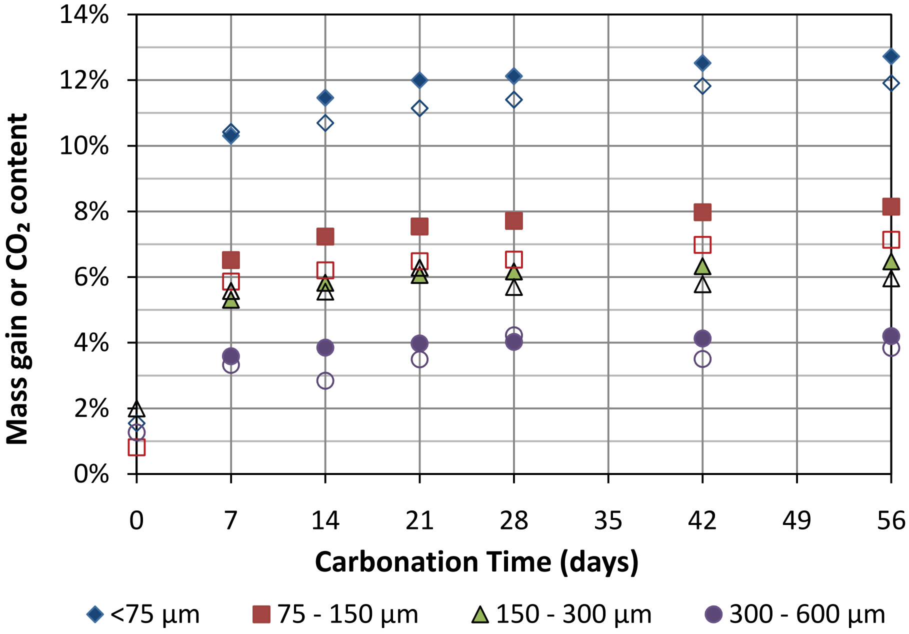

Figure 4.8: Mass gain (solid symbols) and CO_2 content by IR (open symbols) from atmospheric carbonation of sieved ladle slag

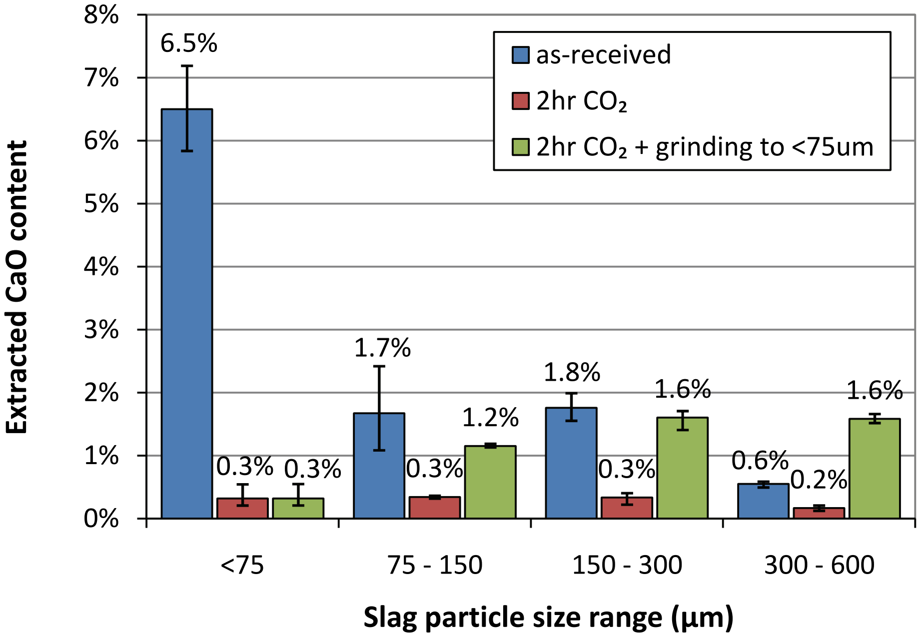

Figure 4.9: Extracted CaO content of as-received slag, carbonated slag and ground carbonated slag

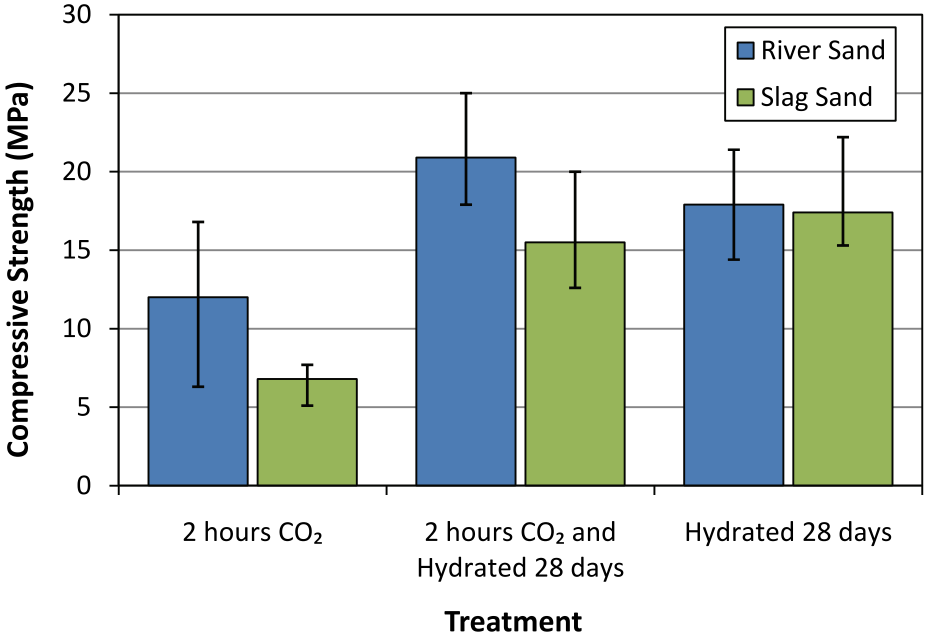

Figure 4.10: Compressive strength of mortars

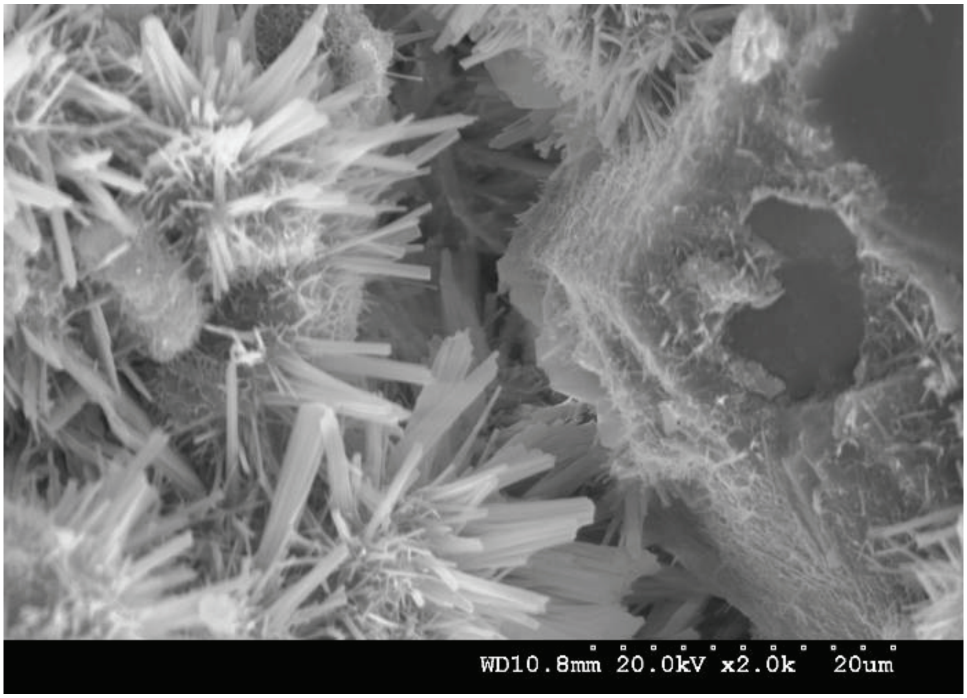

Figure 4.11: SEM image of a 28-day hydrated mortar with river sand

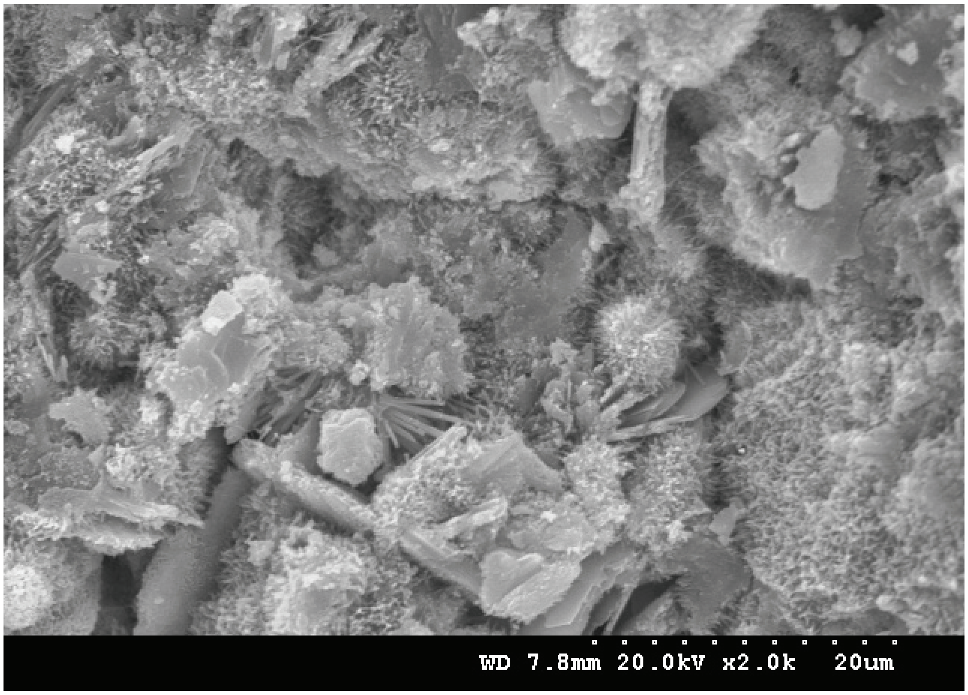

Figure 4.12: SEM image of a 28-day hydrated mortar with carbonated slag sand

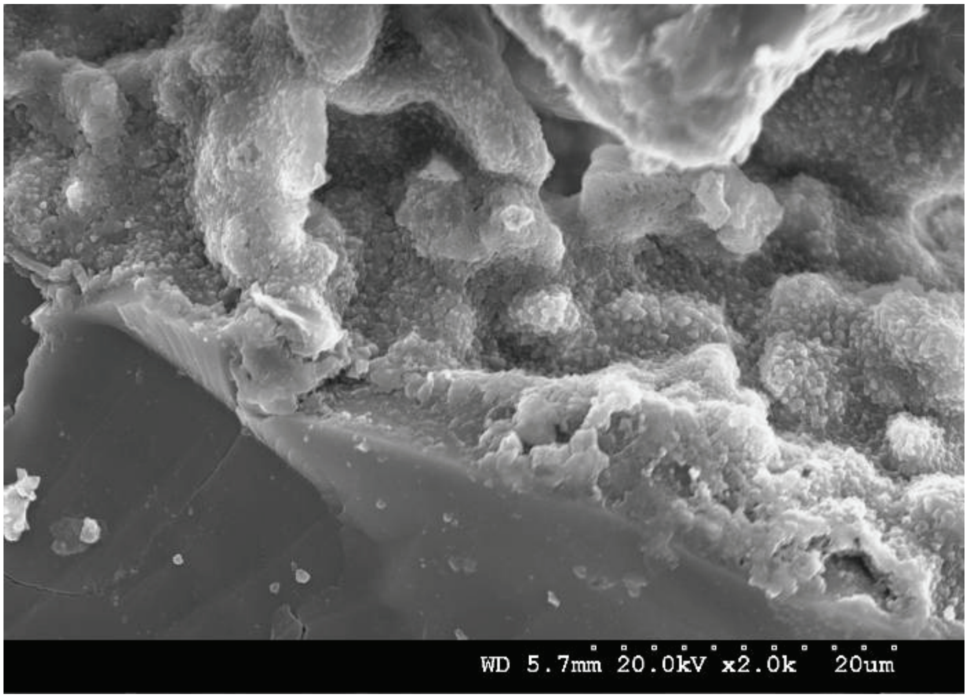

Figure 4.13: SEM image of a 2-hour carbonation-cured mortar with river sand

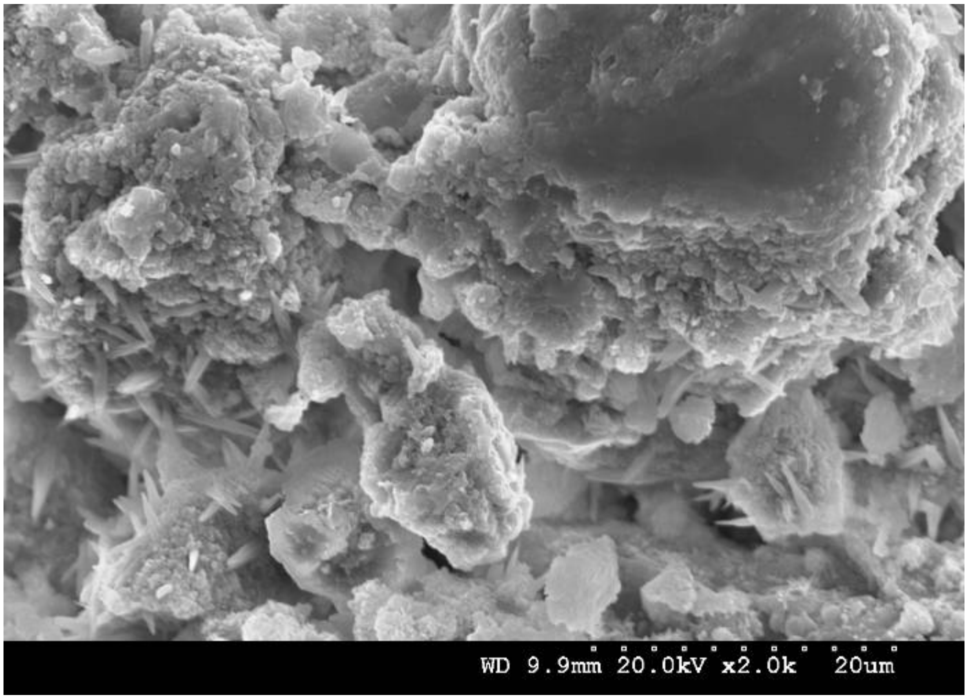

Figure 4.14: SEM image of a 2-hour carbonation-cured mortar with slag sand

Chapter 5

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CARBONATION CURING OF SLAG-CEMENT CONCRETE FOR BINDING CO_2 AND IMPROVING PERFORMANCE

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Sean Monkman and Yixin Shao

PREFACE

Another approach to maximize CO_2 uptake in concrete is to reduce the cement content in the concrete and thereby increase the net gain in sequestration. It was found that the percentage carbon uptake (on the basis of the amount binder based) is limited to fraction of the potential maximum, irrespective of the cement content used. Therefore it is possible to replace cement by ground granulated blast furnace (GGBF) slag to achieve an equivalent carbon uptake at an early age through curing, and an improved late age performance through a subsequent hydration. GGBF slag was selected because it is a commonly employed cement replacement that is less reactive to early age carbonation and can offer long term cementitious behavior. The two primary aims of this chapter are to assess the amount of carbon dioxide absorbed by a concrete sample through carbonation-curing and the effect of the carbonation on the properties.

The research considers the use of blended binders. A commercial slag cement (with a slag content of about 15%) is used as well as OPC/GGBF slag blends with 25% and 50% cement replacement. The concrete industry uses the substitution of cement by secondary cementititious materials (SCMs), such as ground granulated blast furnace slag, as a sustainability measure. If carbon dioxide sequestration is intended to create concrete with a reduced environmental impact, then it is important to consider an accepted and conventional way of achieving this goal through slag blends.

The gas pressure of 150 kPa was selected after testing showed that there was only a small difference between carbonation uptake at a gas pressure of 500 kPa and at a pressure of 150 kPa. Carbonating at a lower pressure is considered to be a lower energy process and it is a relevant consideration for the planned assessment of the process feasibility.

The work is presented in the form in which it was accepted for publication by the ASCE Journal of Materials in Civil Engineering.

ABSTRACT

Early age carbonation-curing of slag cement concrete was investigated to assess the feasibility of binding CO_2 in slag cement building products while improving their short-term and long-term performance. Four binder types were compared: OPC, an 85/15 slag cement, a 75/25 slag blend and a 50/50 slag blend. A two hour carbonation-curing treatment allowed concretes to bind 8-10% CO_2 by mass of binder and attain as much as 82% of the 24-hour hydration strength. The subsequent strength development of carbonated concrete was slower in the first 24 hours possibly due to the carbonate build-up, but was comparable to the conventionally hydrated concrete after 28 days. The carbonated concrete was shown to have a fracture toughness comparable to that of the hydrated concrete. The freeze/thaw durability of the concrete in deicing salt solution was vastly improved by the carbonation treatment. The pH of the carbonated concrete was reduced but was still above the threshold level required for the passivation of iron. The use of slag in carbonation-curing is beneficial to strength gain, shrinkage reduction and deicing salt resistance.

INTRODUCTION

Blends of Portland cement with ground granulated blast furnace (GGBF) slag have been widely accepted as an important contributor to sustainability in the concrete industry. Blended cements require less energy for producing binders for concrete, utilize industry waste for benefits and improves durability of concrete made of the blends (Parissi and Frigione 2003). It was also reported that the early strength development of slag-cement blends was slow, the atmospheric carbonation rate was higher and initial scaling damage due to freeze-thaw cycling was more significant (Osborne 1999).

Carbonation-curing of cementitious materials has been studied for accelerating strength gain (Berger et al. 1972) and for their ability to bind carbon dioxide (Monkman and Shao 2006). A two-hour carbonation-curing (using CO_2 at 500 kPa and a w/b of 0.15) of Portland cement was found to be able to achieve a carbonation degree of about 25% with a strength of 50 MPa, while GGBF slag reached a carbonation degree of 18% with a strength of 8 MPa. Carbonation-curing could improve the early age strength gain and address that limitation of slag-cement binding systems. Since carbonation-curing is a CO_2 consuming process, it can be integrated into a global greenhouse gas emission reduction scheme to offer a beneficial use of as-captured or recovered $CO_{2.}$

Weathering carbonation and its associated corrosion problems in reinforced concrete have been widely studied (Richardson 1988). It is a slow reaction between calcium compounds and carbon dioxide in the air and can happen to concrete throughout its entire service life. Blended slag-cement concretes exposed to this type of carbonation have been associated with higher carbonation rates (Osborne 1999) which can lead to lower compressive strengths (Sulapha et al. 2003) and increase the risk of steel corrosion in concrete due to the reduction in pH values to as low as 8.5 (Gjorv 1989).

Carbonation-curing is different from weathering carbonation in that the former is applied at a very early age while the latter occurs in matured concrete. This research aims to investigate carbonation-curing as a way of simultaneously binding carbon dioxide into slag-cement concrete products and improving their performance. The blended cements are attractive from a net carbon uptake standpoint because of the reduced cement content, and from a long term performance standpoint because of their latent cementitious reactivity. It is expected that carbonation-curing would provide the slag cement concrete with higher early strength and the subsequent hydration would contribute to the later development of strength and durability. Research on the long term performance of carbonation-cured concrete is scarce. Carbonated concretes have been observed to show greater brittleness (Jerga 2004) and carbonated mortar has shown slower later strength gain due to the build-up of carbonation products (Hannawayya 1984). These issues will also be examined.

This research program investigated the carbonation behaviour of blended slag-cement binders and their concretes. The binders were assessed in powder form in terms of the degree of carbonation and hydration. Concrete was assessed in compact form in terms of strengths at different ages, toughness, pH change, atmospheric carbonation shrinkage, and deicing salt freeze/thaw durability.

EXPERIMENTAL

The Materials

Three cementitious binders, a Type 10 cement, a commercial slag cement containing about 15% GGBF slag, and a ground granulated blast furnace (GGBF) slag, were used alone or in blends. The chemical compositions of the cement, slag cement, and GGBF slag were determined using XRF and are presented in Table 5.1. The specific surface area of the three materials was 373, 517 and 424 m^2/kg, respectively. The CO_2 content of each of the as-received materials was about 0.5%. The capacity for the cementitious materials to bind carbon dioxide is related to their chemistry and is expressed as a mass gain as estimated by the Steinour formula (Steinour 1959). The cement had a carbonation capacity of 49.6%, the slag cement 49.4%, and the GGBF 40.7%.

The fine aggregate used in the concrete batches was a river sand with a fineness modulus of 2.53. The coarse aggregate was crushed granite prepared by crushing 6 mm (¼ in) stone with a jaw crusher and collecting the fraction that passed through a 4.75 mm sieve but was retained on 2.36 mm. The CO_2 content of the granite, as determined by combustion and infrared analysis, was 0.36%. Granite was selected to minimize the presence of carbonates in the aggregates.

Carbonation-curing

Carbonation-curing was conducted in a Model 1500 15 Bar Pressure Plate Extractor, (Soilmoisture Equipment Corp). A schematic of the accelerated carbonation reactor is shown in Figure 5.1. Concrete samples were placed in the chamber which was evacuated to about 50 kPa below atmospheric pressure to remove the air. The chamber was then filled with CO_2 of 99.5% purity to a pressure of 150 kPa and maintained at the set pressure for 2 hours. The chamber was filled such that the ultimate gas pressure was achieved within 45 to 60 seconds. The gas was considered to be analogous to carbon dioxide recovered (and purified) from an industrial source such as flue gas. A constant supply of gas ensured that any carbon dioxide that was consumed by reaction with the sample was immediately replaced with fresh gaseous CO_2. A thermocouple was placed in contact with one of the samples. The temperature, initial mass and final mass of the specimen was recorded. Any water rejected from the sample during carbonation (due to exothermic temperature rise) condensed on the interior of the chamber and, at the conclusion of the test, was collected by absorbent paper and quantified. The specimens were removed from the chamber and either tested immediately or hydrated by either storing them in a humid environment or immersing them in saturated limewater solution.

Sample Preparation

Carbonation-curing was performed on two groups of samples: binders in powder form and concrete in compact form. The former was used to examine the interaction of carbonation and hydration and the latter to investigate their mechanical and physical performance in zero-slump concrete products.

In total, five different binders were tested. They were the three as-received binders (Table 5.1) and two cement/ slag blends with either 25% or 50% slag. The five binders were first tested as powders (300 g) mixed with water at a w/b of 0.125. The powder was then either carbonated or hydrated. The carbonated samples were examined either immediately after 2-hour carbonation or after 28 days following hydration in a sealed container with a relative humidity 87%. Hydrated samples were hydrated for 3 days and 28 days.

Four concrete compacts were made with different binders: a Type 10 OPC concrete, slag cement concrete, a concrete with 25% of cement replaced with slag, and a 50/50 blend concrete. The aggregate to binder ratio was 4:1, and the coarse to fine aggregate ratio was 1:1. A water to binder ratio of 0.26 was selected. It was high enough to provide sufficient moisture to allow press-forming of the zero-slump concrete while still using a relatively low water content to promote the carbonation reaction.

Two types of sample of concrete compacts were prepared. Compact blocks of 76 mm (3 in) by 127 mm (5 in) by 20 mm (3/4 in) were used for compact strength, pH and freeze/thaw durability testing. Compact bars of dimensions 25 mm (1 in) square by 279 mm (11 in) long were used for shrinkage testing. The samples were produced by compacting material into moulds with an compression testing machine. The forming load corresponded to a compressive stress of 12 MPa which was determined to be optimal for mass gain and strength in preliminary testing.

Samples were prepared in pairs: half of the batch was ready for hydration and half for immediate carbonation-curing plus subsequent hydration. Samples meant for conventional hydration were placed in a moisture chamber with a relative humidity of 87%. For limewater immersion curing, samples were preset 24 hours before being placed in limewater in a sealed container. The long term hydration by immersion in saturated limewater solution was used to examine the maximum hydration response of any sample.

CO_2 Uptake Quantification

The primary method of quantifying carbonation was by considering the change in the mass of the sample. The CO_2 uptake estimated by mass gain was determined by considering the initial mass, the final carbonated mass (including the lost water) and the total original mass of the dry binder:

$$Mass\ gain\ (\%) = \frac{Mass_{final} + Mass_{water\ loss} - Mass_{initial}}{Mass_{dry\ binder}} = \frac{\Delta Mass_{CO_2}}{Mass_{dry\ binder}} \quad (1)$$

The water is included in this calculation because the carbonation test was treated as a closed system. It is assumed that the only water present at the conclusion of the carbonation treatment had been present in the chamber at the beginning of the test as mix water. The aggregates are excluded because they do not absorb CO_2. If the increase in mass during the carbonation was solely due to the incorporation of carbon dioxide into solid carbonation products then a measure of the mass gain of the closed system can provide an effective estimate of CO_2 uptake.

The validity of using mass gain as a way of quantifying mass gain was examined in the tests of powder binders using Berger's pyrolysis approach (Berger et al. 1972). Carbonated or hydrated powder samples of 50 grams were placed into ceramic crucibles and were oven dried at 105 °C to remove any uncombined water. The samples were then heated in a muffle furnace to 540 °C and 980 °C. It is understood that the mass loss from 105 °C to 540 °C is attributable to the loss of chemically bound water which can be used to estimate the hydration products such as calcium silicate hydrate and calcium hydroxide. The subsequent mass loss to 980 °C is attributable to chemically bound carbon dioxide. The mass losses were normalized over the sample's ignited mass (the mass following heating to 980 °C) to allow for comparisons between anhydrous and hydrated samples. The quantification of hydration products would possibly exclude ettringite, which can decompose below 100 °C (Wang et al. 2004), therefore the thermal analysis does not necessarily permit the degree of hydration to be determined. The quantification of the carbonate content by thermal analysis was expected to closely approximate the mass gain if the latter technique was a valid approach. Thermogravimetric analysis was not performed because the technique uses a very small sample size and presents difficulties in assessing the overall carbon content of concrete.

Compressive Strength Testing

Carbonated samples were tested immediately after the two-hour carbonation as well as after a subsequent hydration of 24 hours, 28 days and 120 days. Reference samples were tested after hydration in a moist environment up to 24 hours, 28 days, or 120 days. The samples tested at 24 hours were permitted to rest exposed at room temperature (23 ±2 °C) on a laboratory bench for one hour prior to testing while samples tested at greater ages were allowed to air out for 24 hours prior to testing. For each batch, five samples were tested and the results averaged. The samples were loaded across their length such that the cross sectional area was 127 mm long by 25 mm thick.

Accelerated Weathering Tests

Carbonation shrinkage specimens were created in batches of three bars with dimensions of 25.4 mm by 25.4 mm by 279 mm long. Accelerated weathering testing started after 58 to 60 days of hydration in a moist environment. Upon the completion of the hydration, the samples were allowed to remain exposed on the laboratory bench for 24 hours. Stainless steel discs approximately 5 mm in diameter were affixed to the bars using epoxy adhesive. Two discs were attached 203.2 mm (8 in) apart centre to centre down the middle of the bar. Depressions in the centre of the discs were used by a demountable mechanical strain gauge (DEMEC) to obtain a length measurement accurate to 0.00254 mm (0.0001 in). After allowing the epoxy to set for 1 hour, the length of each bar sample and mass of every sample was recorded.

A polyethylene tank was used as a chamber for accelerated weathering carbonation testing. The chamber contained plastic perforated shelves to support the specimens and a fan that provided circulation to maintain a consistent humidity and carbon dioxide concentration throughout the chamber.

The concentration of carbon dioxide in the chamber was monitored using a Quantek Instruments Model 906 Carbon dioxide Analyzer. Gas flow through the analyzer was generated with the pump from the dehumidification system. The chamber was flushed with CO_2 to create an environment of 50% CO_2 concentration at atmospheric pressure. The relative humidity of the chamber was controlled at about 65% to promote carbonation at the maximum rate (RILEM Recommendations 1988) by providing enough moisture for the carbonation reactions for proceed but not so much water to saturate the concrete pore network and prevent gas ingress. A schematic of the accelerated carbonation weathering chamber is shown in Figure 5.2.

The samples were removed from the chamber periodically for length measurements. Following all measurements, the chamber was sealed, the carbon dioxide concentration was returned to 50% and the humidity was returned to 65%. The lengths of the samples were measured frequently over a weathering carbonation exposure time of 91 days. The carbonation shrinkage strain was calculated.

pH and Absorption Tests

A leaching method was used to determine the pH of pore solution in the cement paste of the concrete samples. Entire concrete compacts were placed in individual containers filled with distilled water. The pH of the water was measured before the sample was added and one hour after the sample was added. Measurements were made regularly after the test started and continued for 42 days. Two specimens were tested per batch of concrete and the samples were hydrated for 28 days before pH testing.

The absorption of the concrete samples was tested according to ASTM Standard C140 (ASTM 2005). The samples were immersed in room temperature water for 24 hours before measuring the saturated surface dry mass and the oven dried mass. The samples were tested after hydration to 28 days.

Freeze/Thaw Testing

Deicing salt freeze/thaw durability testing was performed according to Canadian Standards Association (CSA) A231.2-95 for Precast Concrete Pavers. The concrete specimens were hydrated for 56 days before the freeze/thaw testing started. For each binder type, three carbonation-cured and three hydrated samples were tested. The specimens were brushed clean of any loose material and oven-conditioned for 48 hours at 60 °C before they were placed in individual plastic containers with a volume less than three times the sample volume. The container was filled with a 3% sodium chloride solution to a depth of 5 mm above the top of the sample. After a 24-hour saturation period, the samples were subjected to cycles of freezing for 16 ±1 hours and thawing for 8 ±1 hours. During the freezing cycles, the samples were stored in a freezer at -15 °C. The samples were thawed at room temperature by placing them on a laboratory bench. Following 10 and 25 complete freeze/thaw cycles, each specimen was photographed and its mass loss was determined by rinsing specimens with deionized water over a 75 μm sieve. Any loose particles that were washed from the samples, as well as any loose particles found in the specimen containers, were collected and oven-dried. The dry mass of the collected material was recorded. A sample was judged to fail if its cumulative mass loss per surface area after 25 cycles exceeded 200 g/m^2.

RESULTS AND DISCUSSION

Carbonation and Hydration of Slag-cement Blends

Binder blends were tested by thermal analysis to study the role carbonation played in the early and subsequent hydration and to examine whether the mass gain was a suitable estimate for the carbon content. The results of the powder testing are summarized in Table 5.2. It was found that binder powders carbonated for 2 hours had gained an amount of bound water that was close to what was gained in a sample hydrated for 3 days. The ratio of the amount of bound water in the 2 hour carbonated samples compared to the 3 day hydrated samples was 74%, 72%, 84% 100% and 156% in the OPC, slag cement, 75/25 blend, 50/50 blend and GGBF slag respectively. This suggested that the percentage hydration product created by 2-hour carbonation and by 3-day hydration was comparable. The hydration process was increasingly accelerated as the cement content was reduced. Hydrating a carbonated sample for 28 days increased the amount of bound water which indicated that the carbonated binders could still form hydration products, although, in each case except for the slag cement, the total amount of hydrates was lower than that in the non-carbonated sample hydrated for 28 days. The reduced hydration in carbonated samples suggested that the carbonation products provided some hindrance on subsequent hydration. The high fineness of slag cement made its subsequent hydration comparable to non-carbonated OPC reference while GGBF slag is much less reactive to carbon dioxide because of its glassy nature.

It can be seen in Table 5.2 that the CO_2 content determined by mass gain was comparable to that determined by thermal analysis. Considering the data, the percentage mass gain was 0.6% higher than the percentage carbonate content. The carbon content obtained 28 days after carbonation showed that the sequestered CO_2 was stable in a carbonate form. The fact that the mass gain is consistently higher than the mass loss associated with carbonate decomposition suggests the presence of carbonate phases decomposing at temperatures lower than 540 °C (Kroone and Blakey 1959). It is concluded that the mass gain, however, provides a reasonable estimate of the increase in carbon content resulting from carbonation-curing. It is appropriate to use a straightforward and direct approach of measuring the carbonation uptake of concrete since the binder cannot be easily separated from the other components in the concrete mixture. Additionally, the measurement assesses the entire specimen rather than a cored sample.

Carbon Uptake in Concrete

The carbonation mass gain, water loss and peak temperature results for the concrete compacts are summarized in Figure 5.3. The error bars represent the range of test results for 7 different batches. It can be seen that the mass gain ranged from an average of 8.7% in the slag cement up to 10.5% for the 50/50 blend. In comparison to the powder test results (Table 5.2), carbon uptakes by concrete compacts are of the same order as by loose powder. It implies that reactivity is not proportional to the cement content and that porosity of concrete may not be an important factor on reactivity. The average water loss for the samples ranged between 13 and 17% and the average peak temperature ranged between 32 to 35 °C, indicating the degree of carbonation of the four concretes was of the same order.

To understand the contribution of slag to the carbonation reaction in a blend of more reactive cement and less reactive slag, an investigative trial was performed with a concrete sample made with a blended binder of 50% anhydrous cement and 50% carbonated cement. The carbonated cement was pre-carbonated with a water/binder ratio of 0.12 and carbonated for 4 hours at 150kPa to give a carbonation mass gain of 12.8%. This pre-carbonated cement was analogous to the slag which possessed a fineness comparable to the anhydrous cement while being much less reactive to CO_2 than anhydrous cement. Since half the binder had been previously carbonated, a reasonable was that this sample would have a carbonation mass gain close to half that of the 100% OPC binder sample. Instead, the mass gain was the same (9.3% for this test compared to an average of 9.3% for seven carbonated OPC concretes in the main study) although it produced a much weaker concrete (4.0 MPa compared to 8.8 MPa after 2 hours of carbonation). It is concluded that the slag and the carbonated cement, both being less reactive than anhydrous cement, effectively dispersed the cement particles. A schematic is shown in Figure 5.4. The dispersed cement particles (white circles) carbonated more (had a larger build up of carbonated products represented in grey) when the less reactive slag (or pre-carbonated cement, dark circles) was present (Figure 5.4b). If only cement is used as the reference denominator in Equation 1, the reactivity of cement in the 50/50 blend is twice as much as the cement in the OPC concrete. The slag either allowed the vigorous carbonation of cement to take place with fewer competitive sites in which a cement particle was adjacent to another cement particle or the CO_2 penetrated deeper into the sample before ingress was slowed by the buildup of carbonation products. However, the strength was reduced due to the lack of a continuous matrix. While dispersing the anhydrous cement particles might allow for more carbonation to occur, the development of effectively strong and uniform carbonated microstructures in 50/50 blend was hindered.

Compressive Strength and Toughness

The strength data for concretes tested after three early age treatmet (carbonated for 2 hours, carbonated for 2 hours with additional hydration to 24 hours, and hydrated for 24 hours) is presented in Figure 5.5 (error bars represent highest and lowest of 5 samples tested). Table 5.3 summarises the proportion of strength relative to the 24 hour strengths concretes that was achieved after carbonation for 2 hours. All of the four binder types achieved more than 70% of the 24 hour hydration strength after 2 hours of carbonation-curing with the carbonated 50/50 blend concrete showing the highest proportion at 106.6%. The strength development at 24 hours showed that the carbonated concretes, except for the 50/50 blend, were slightly weaker than the hydrated concretes. The difference was more significant in OPC concrete than in blended cement concrete. The ratio was 86% in OPC versus 95%, 95% and 142% in 85/15, 75/15 and 50/50 blend concrete respectively. It is apparent that the use of slag increases the subsequent hydration capacity after early carbonation. This phenomenon was observed again in the 28 day strength data, as shown in Figure 5.6 (error bars represent highest and lowest of 5 samples tested). Therefore, carbonated OPC concrete had shown a slower hydration than its hydrated counterpart. The strength ratio of the carbonated to the hydrated concretes at 28 days was 87.2%, 102.1%, 102.8% and 95.7%, respectively, for OPC, slag cement, 75/25 blend and 50/50 blend. While strengths in carbonated 85/15 blend (slag-cement) and 75/25 blended cement concretes exceeded their hydrated counterparts as well as their reference OPC hydrated reference, 50/50 blend showed slower reaction in carbonated samples than in the hydrated samples. It shows that the use of slag is beneficial to carbonation-cured concrete. The subsequent hydration in carbonated concrete was faster in low slag concrete (up to 25%) and slower in high slag (up to 50%) substitution. For the concretes containing slag, the strengths of the concretes decreased as the percentage of slag increased.

The strength results after 120 days of curing (both moist curing and limewater curing) are presented in Figure 5.7 (error bars represent highest and lowest of 5 samples tested). For moist curing, the slag cement concretes were the strongest and showed no significant difference between the carbonated and hydrated samples at a 95% confidence interval. The carbonated concretes were significantly stronger for the OPC and 75/25 blended concretes. Only the carbonated 50/50 blend concrete compared unfavourably with its counterpart. It was also the only carbonated concrete that was weaker than the OPC hydration reference. Similar trends are seen for the concretes hydrated for 120 days in limewater. The carbonated concretes were stronger than the hydrated concrete in all cases but the 50/50 GGBF slag blend. A comparison of the two 120-day strengths, hydrated in a moist environment compared to the samples immersed in limewater, is presented in Table 5.4. For two of the samples, the carbonated 50/50 blend and the hydrated slag cement concrete, their strengths were not significantly different. In all other cases the limewater hydration significantly increased strength. For the concretes in which the increase in strength was significant, the average improvement was 38.3% with the increase being about equal whether the concrete had been carbonated first (38.9%) or only hydrated (37.6%). This indicates that the lack of water was responsible for the slow strength development and the build-up of carbonate products did not impact the long-term hydration ability as long as there was sufficient water supply.

The large increase in strength of the carbonated concretes hydrated for 120 days in saturated limewater solution shows that the carbonated concretes have a significant capacity for strength development related to hydration. A comparison of the strength at 2 hours and at 120 days in limewater of the carbonated concretes showed that the strength of the OPC concrete increased 247%, the 75/25 GGBF slag blend concrete strength increased 256%, the slag cement concrete strength increased 190% and that of the 50/50 GGBF slag blend concrete by 148%. Thus, to follow a carbonation-curing treatment with an additional hydration step, such as a sprayed water treatment, would combine the benefit of CO_2 absorption with a conventional hydration approach for both early and late strength development.

The results for fracture toughness of all concretes hydrated for 120 days in the moist environment are summarised in Table 5.5. Each number is the average of five values. For each concrete, the area under the stress-strain curve was determined and defined as the fracture toughness. This was intended to examine if carbonated concrete was more brittle than the non-carbonated reference. A statistical test of significance suggested that the carbonated OPC concrete had higher fracture energy and was less brittle than its hydrated reference. There was no significant difference between the fracture toughness of the carbonated and hydrated concretes for the other three binder types at different ages. The typical stress-strain curves for OPC concrete and slag cement concrete subjected to hydration and carbonation are presented in Figure 5.8. The mechanical responses of carbonated and hydrated concretes at 120 days are reasonably close.

The contribution of GGBF to the strength development of the concrete was examined by comparing the 120 day strength (both moist-cured and immersed in limewater) to the strength of the concrete at 28 days. The increase in strength gave an indication of whether the carbonation-curing adversely affected the secondary cementitious nature of the slag. It can be seen in Table 5.6 that the long term strength development of the carbonated concretes was either close to, or exceeded the strength development of, the hydrated concrete in all cases except for the 50/50 blend. It is likely that the carbonated cement could provide significant long-term chemical activation of the slag given a sufficient water supply.

Freeze/thaw Performance

The freeze/thaw performance of the carbonated concrete was markedly better than that of the hydrated concrete. The results are summarised in Table 5.7. After ten cycles, deicing salt scaling had occurred in at least one specimen in every batch of the three hydrated specimens while none of the carbonated specimens had shown any significant mass loss. All of the hydrated specimens had completely disintegrated before 25 cycles while none of the carbonated samples had a mass loss that exceeded the failure criteria. There is strong evidence that the carbonation induced surface crystallization could strengthen the concrete's resistance to freeze-thaw scaling.

pH and Absorption

The pH of the carbonated concrete was reduced in each of the five types of concrete. The results are summarized in Table 5.8. The pH of the carbonated concretes were lower than those measured for the hydrated concretes. The carbonated OPC, slag cement and 75/25 GGBF slag blend each had a pH of about 12.2. The GGBF slag blend with 50% cement replacement had the lowest pH of 11.6. The carbonation treatment lowered the pore solution pH but the results of the present treatment suggest that the pH reductions would not necessarily be large enough to cause concern about depassivation of steel and the attendant corrosion problems.

The water absorption results are presented in Figure 5.9 which examines if the early carbonation deteriorated the hydraulic activity of cement through the carbonate build-up and the loss of absorption capacity. For each of the four types of binder, the percentage absorption of the carbonated concretes was only about 0.6% lower than that of the hydrated concretes. It shows that the water uptake behaviour of carbonated concrete was not significantly altered and their subsequent hydration should not be negatively affected by the early carbonation.

Weathering Shrinkage

The average ultimate shrinkage of each of the eight batches after 91 days accelerated weathering carbonation exposure is presented in Table 5.9. For all binders except for the Type 10 OPC, the accelerated weathering carbonation shrinkage was smaller for the carbonation-cured samples than for the hydrated samples. Neither the OPC concrete nor the slag cement concrete showed a significant difference in the shrinkage as compared between the hydrated and carbonation-cured specimens. Both carbonated and hydrated slag cement concretes exhibited excellent shrinkage resistance with slightly more shrinkage reduction occurring with the carbonation treatment. For the two slag blends, 75/25 and 50/50, the carbonation-cured concrete had significantly lower shrinkage than the hydrated concrete. The carbonation-curing reduced the average weathering shrinkage by 50% for the 75/25 blend and 43% for the 50/50 blend. This phenomenon had been studied by the masonry block industry and was employed as a post-steam-curing treatment to improve the service shrinkage resistance (Toennies 1960). The use of slag in carbonation-cured concrete is more beneficial. The carbonated slag-cement concretes of different blend ratios had much lower shrinkage than the carbonated OPC reference concrete. Additionally, the hydrated 75/25 and 50/50 blend concretes did not show a noticeable shrinkage reduction in comparison with the hydrated OPC reference. Therefore, early carbonation of slag concrete could offer excellent resistance to weathering carbonation shrinkage.

CONCLUSIONS

The carbonation-curing of concrete products allowed for significant binding of CO_2 while improving the properties of the concrete. The absorption of carbon dioxide, by mass of binder, was approximately 8 to 10%. The carbonation treatment gave the concrete strength within two hours that was more than 70% of the 24 hour hydration strength. The strength gain of carbonated concrete was, however, slower beyond 24 hours additional hydration, possibly due to the carbonate build-up. Longer subsequent hydration resulted in carbonated concrete with strengths comparable to those of normal hydrated concrete, although the carbonation treatment of the 50/50 blend concrete reduced the cementitious nature of the slag. The fracture toughness of the carbonated and hydrated concretes were comparable when tested after 120 days of hydration. The carbonation treatment enormously improved the freeze/thaw durability. pH values of the carbonated concrete was reduced but was still above the level required for the passivation of iron. Significant improvement in the weathering shrinkage resistance of concretes with 25% or 50% GGBF slag was observed.

GGBF slag was used to reduce the cement content and improve the net gain in CO_2 emission reduction. The addition of slag did not affect the carbon dioxide uptake by concrete. Instead, the use of slag was generally beneficial. The carbonated slag-cement concretes with 15% and 25% slag had higher strength than comparable hydrated concretes at ages of 28 and 120 days, and they demonstrated better resistance to weathering carbonation and to freeze/thaw scaling and maintained pH close to that of the hydrated OPC reference.

Early carbonation is distinct from weathering carbonation. The carbonation degree in 2 hours is about 16-20%. It is modest but still significant, and it occurs in a short period of time and is followed by subsequent hydration. The concrete so produced is comparable, or superior, to normal hydrated concrete and can be used even in reinforced concrete structures with steel reinforcement. The carbonate build-up, the low water-to-cement ratio used in the mixture design and the loss of water during carbonation may contribute to the slow subsequent hydration. Sufficient moisture supply is necessary for continued hydraulic and secondarily cementitious reactions.

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TABLES

Table 5.1: XRF Chemical analysis of the cementitious materials

Species	Type 10 OPC	Slag cement	GGBF slag
CaO	63.1	59.2	38.5
SiO_2	19.6	22.2	40.1
Al_2O_3	4.9	5.7	7.8
MgO	2.0	4.1	9.7
Fe_2O_3	2.0	1.9	0.7
Na_2O	0.85	0.28	0.38
K_2O	-	0.88	0.53
SO_3	3.8	5.06	2.21
CO_2	0.54	0.45	0.49
LOI	2.8	0.83	0.22

Table 5.2: Carbonation and hydration of binder powders

Binder	Factor	Hydrated		Carbonated	
		3 days	28 days	2 hrs	28 days
OPC	Bound H_2O	4.5%	6.2%	3.3%	4.6%
	Bound CO_2	1.2%	1.6%	9.4%	10.7%
	Mass gain	-	-	10.5%	
Slag cement	Bound H_2O	4.3%	5.4%	3.1%	5.3%
	Bound CO_2	1.3%	1.8%	10.3%	10.1%
	Mass gain	-	-	11.8%	
75/25 blend	Bound H_2O	4.1%	5.2%	3.4%	4.5%
	Bound CO_2	0.9%	1.4%	9.8%	10.0%
	Mass gain	-	-	10.3%	
50/50 blend	Bound H_2O	3.8%	5.5%	3.8%	3.9%
	Bound CO_2	1.3%	1.2%	9.8%	9.5%
	Mass gain	-	-	9.7%	
GGBF slag	Bound H_2O	1.0%	1.5%	1.5%	2.6%
	Bound CO_2	0.6%	0.7%	4.2%	3.9%
	Mass gain	-	-	4.6%	

Table 5.3: Comparison of 24-hour concrete strengths

Binder	C/H	C/CH	CH/H
Type 10 OPC	77.7%	90.9%	85.5%
Slag cement	78.4%	82.6%	94.8%
75/25 blend	82.3%	86.6%	95.0%
50/50 blend	106.6%	74.9%	142.3%

Note: C = 2 hr carbonation, CH = 2hr carbonation + 22 hr hydration; H = 24 hr hydration.

Table 5.4: Ratio of 120-day strengths of concretes cured in limewater, $(f'_c)_{LW}$, to concretes cured in a moist environment, $(f'_c)_{MO}$

Binder	Treatment	$(f'_c)_{LW}/(f'_c)_{MO}$
OPC	Hydrated	1.47
	Carbonated	1.37
Slag cement	Hydrated	1.08
	Carbonated	1.35
75/25 blend	Hydrated	1.45
	Carbonated	1.44
50/50 blend	Hydrated	1.20
	Carbonated	0.915

Table 5.5: Fracture toughness of concretes after carbonation and hydration

Binder	Treatment	f'_c (MPa)	Toughness (kJ/m^3)
OPC	2h CO_2	8.84	11.5 ± 0.6
	120d hyd	19.06	34.9 ± 4.6
	2h CO_2 + 120d hyd	22.34	45.8 ± 7.0
slag cement	2h CO_2	11.14	16.7 ± 1.9
	120d hyd	24.64	49.0 ± 3.8
	2h CO_2 + 120d hyd	23.87	49.8 ± 8.8
75/25 blend	2h CO_2	7.75	10.6 ± 1.0
	120d hyd	16.23	29.5 ± 6.4
	2h CO_2 + 120d hyd	19.09	33.5 ± 6.7
50/50 blend	2h CO_2	6.26	7.5 ± 1.4
	120d hyd	19.40	37.8 ± 7.8
	2h CO_2 + 120d hyd	16.92	30.6 ± 4.8

Note: Variability of the toughness expressed as one standard deviation.

Table 5.6: Strength increases for concretes at 120 days compared to 28 days

Concrete	Moist curing		Limewater curing	
	Hydrated	Carbonated	Hydrated	Carbonated
OPC	13.5%	52.7%	67.6%	109.5%
Slag cement	14.4%	8.5%	23.5%	46.6%
75/25 blend	-1.0%	6.8%	43.6%	54.2%
50/50 blend	45.8%	32.9%	75.2%	21.6%

Table 5.7: Results of the freeze/thaw testing for carbonated and hydrated concretes

Binder	Average Mass loss (g/cm^2)			
	After 10 Cycles		After 25 cycles	
	Hydrated	Carbonated	Hydrated	Carbonated
OPC	669.1	6.1	Failed	101.8
Slag cement	192.7	6.1	Failed	145.5
75/25 blend	229.1	6.1	Failed	71.5
50/50 blend	209.7	2.4	Failed	41.2

Table 5.8: Results of pH testing for carbonated and hydrated concretes

Binder	Hydrated	Carbonated
OPC	12.66	12.24
Slag cement	12.65	12.23
75/25 blend	12.62	12.15
50/50 blend	12.57	11.57

Table 5.9: Service carbonation shrinkage of carbonated and hydrated concretes

Binder	Shrinkage (microstrain)		Statistically different
	Hydrated	Carbonated	
OPC	-396 ±142	-425 ±37	No
Slag cement	-137 ±175	-96 ±146	No
75/25 blend	-517 ±29	-258 ±8	Yes
50/50 blend	-317 ±146	-179 ±42	Yes

FIGURES

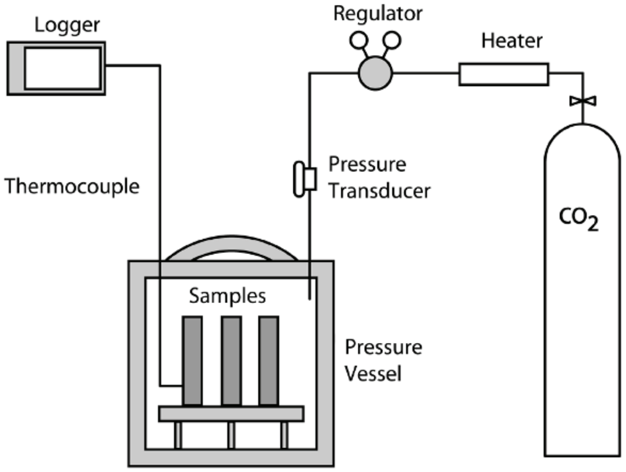

Figure 5.1: Accelerated carbonation setup

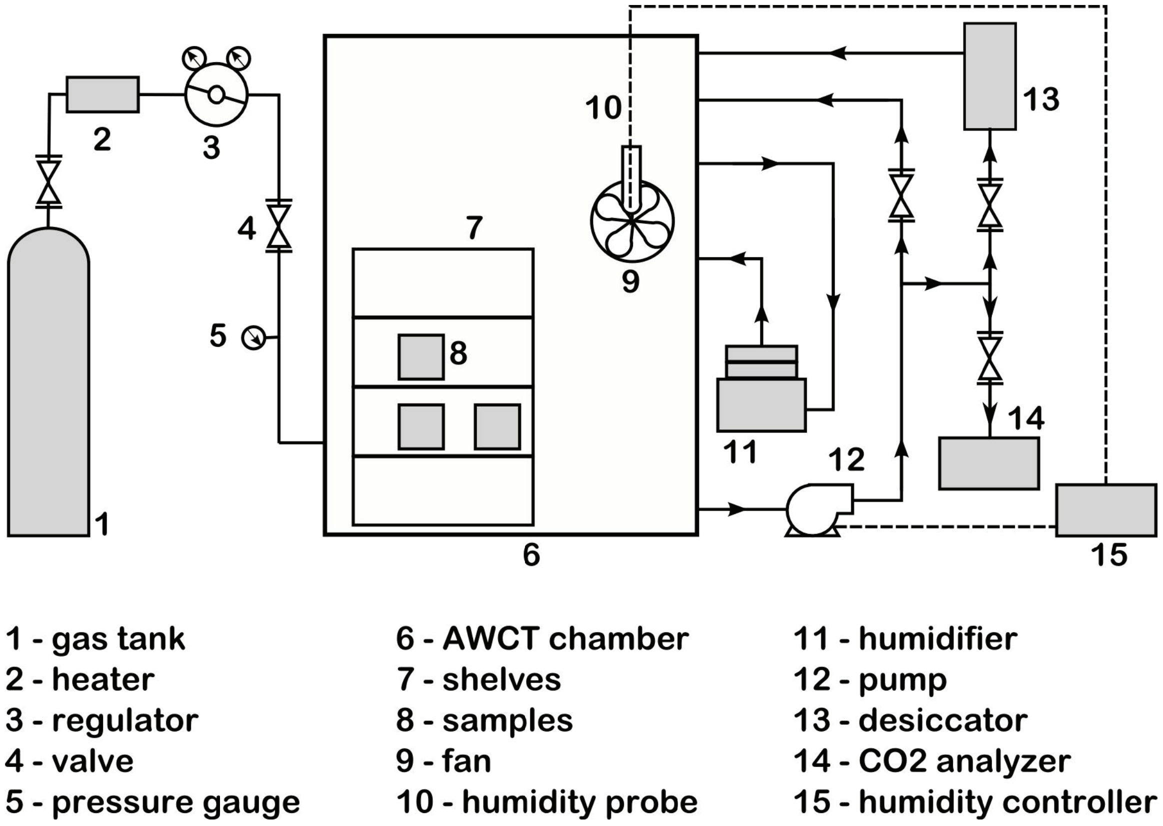

Figure 5.2: Atmospheric weathering carbonation setup

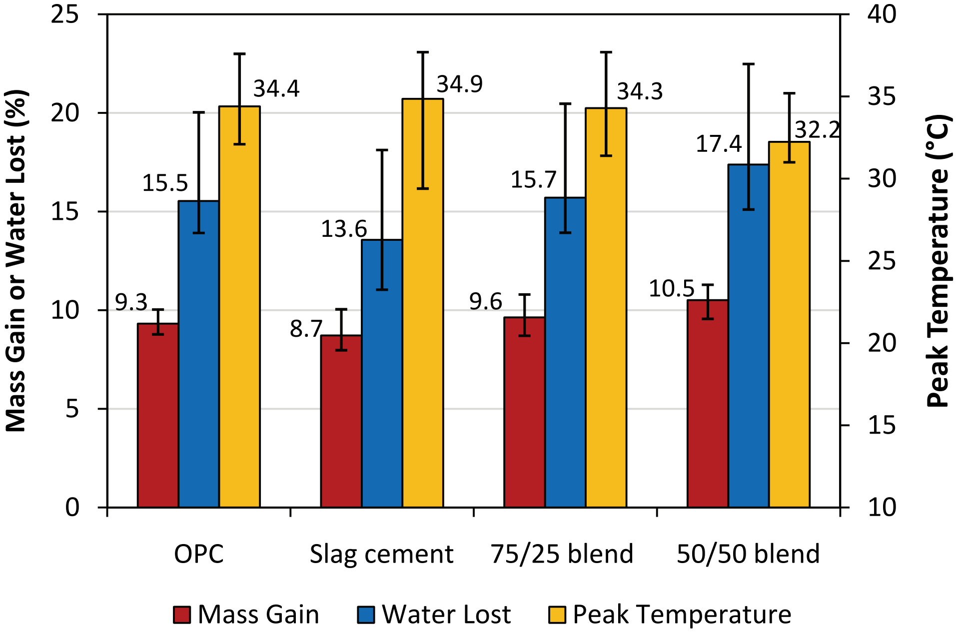

Figure 5.3: Mass gain, water loss and peak temperature of concretes carbonated for 2 hours at a CO_2 pressure of 150 kPa

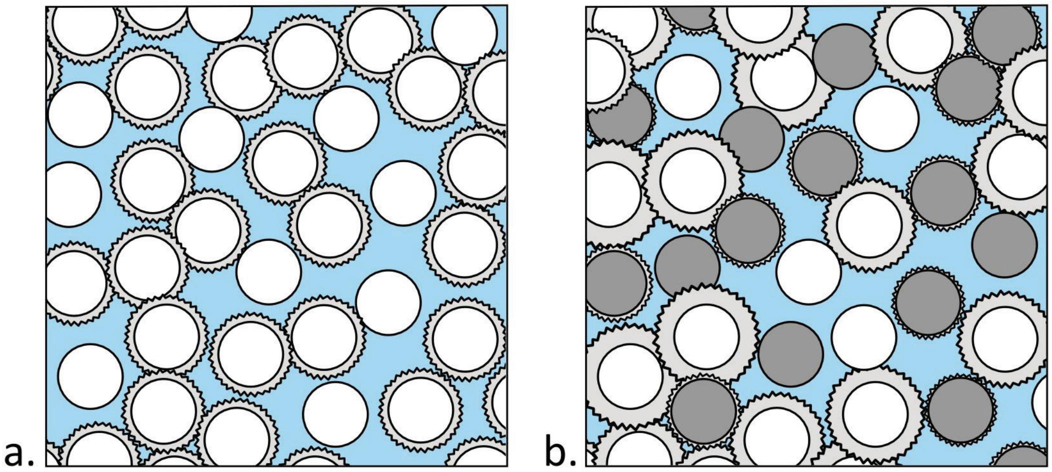

Figure 5.4: Schematic of binders in OPC (a) and in 50/50 blend concrete (b) immediately after carbonation (cement: white circle; slag/pre-carbonated cement: dark circle; carbonation products: grey ring)

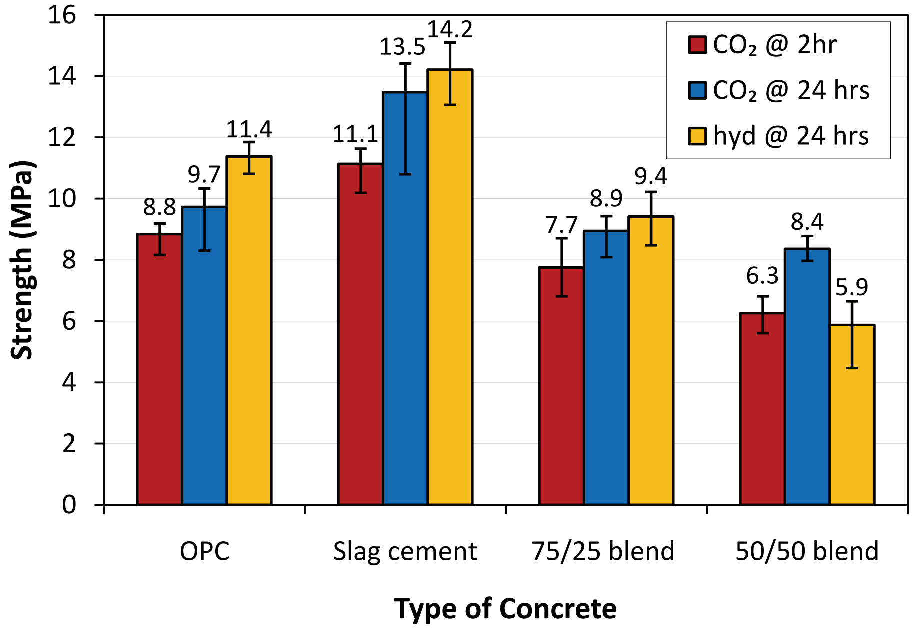

Figure 5.5: Early strength of concretes – carbonated for 2 hours, carbonated for 2 hours and hydrated to 22 hours, and hydrated for 24 hours

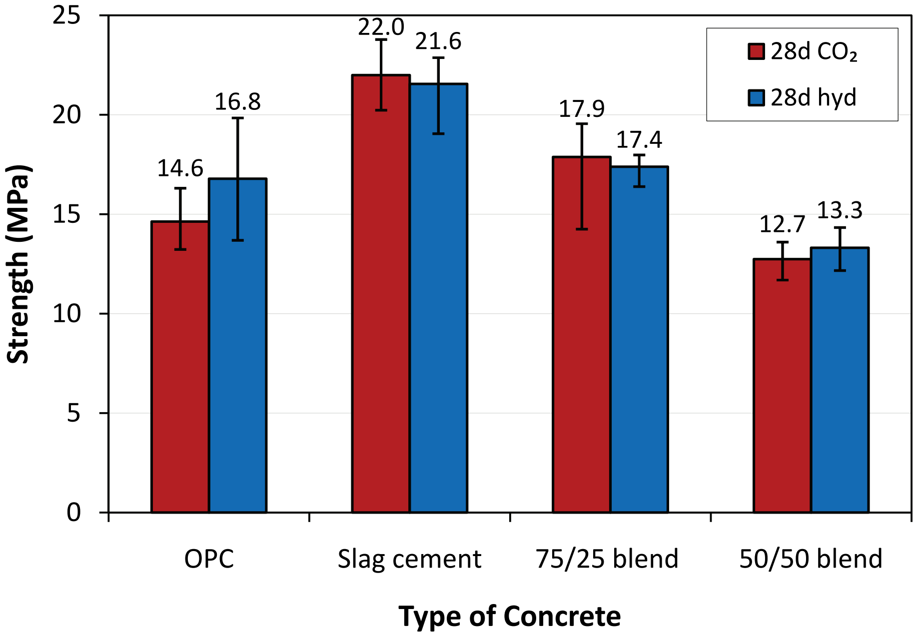

Figure 5.6: 28 day strength of concretes – carbonated for 2 hours prior to hydration and only subjected to hydration

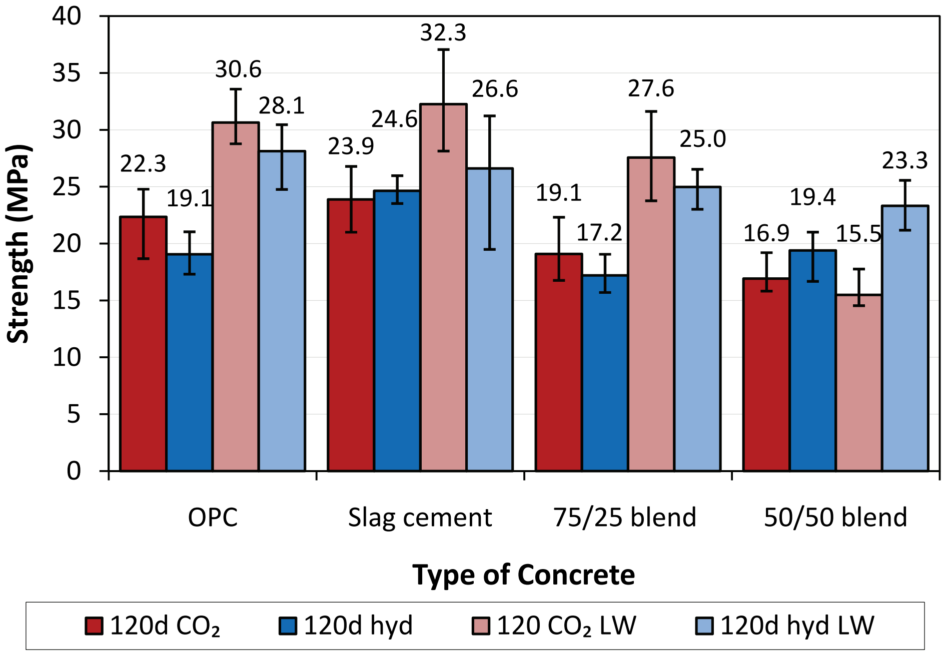

Figure 5.7: Strength of concretes hydrated 120 days in moist environment or in limewater – carbonated for 2 hours prior to hydration and subject only to hydration

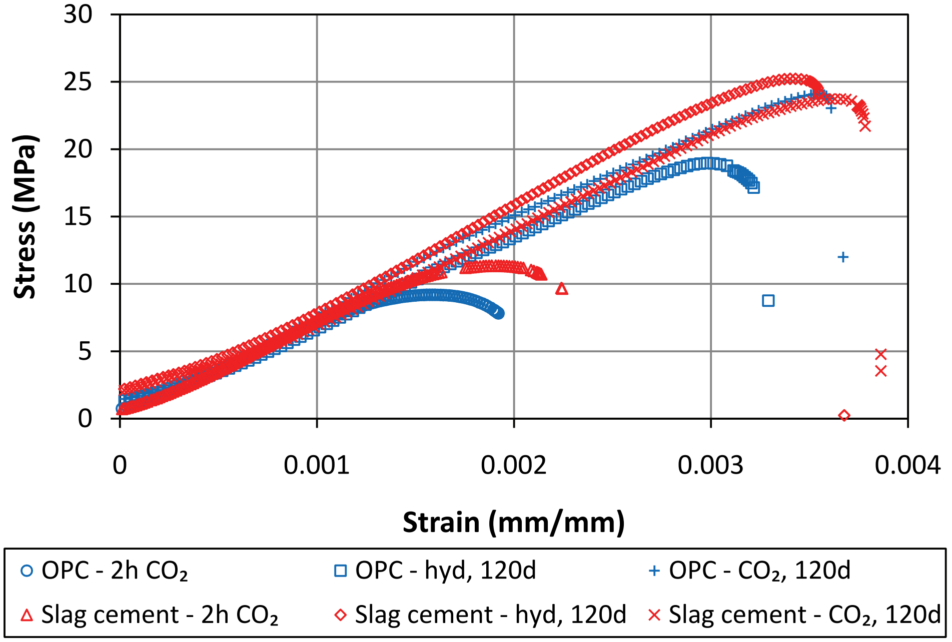

Figure 5.8: Comparison of typical stress-strain curves of slag cement concrete with OPC concrete by carbonation and hydration

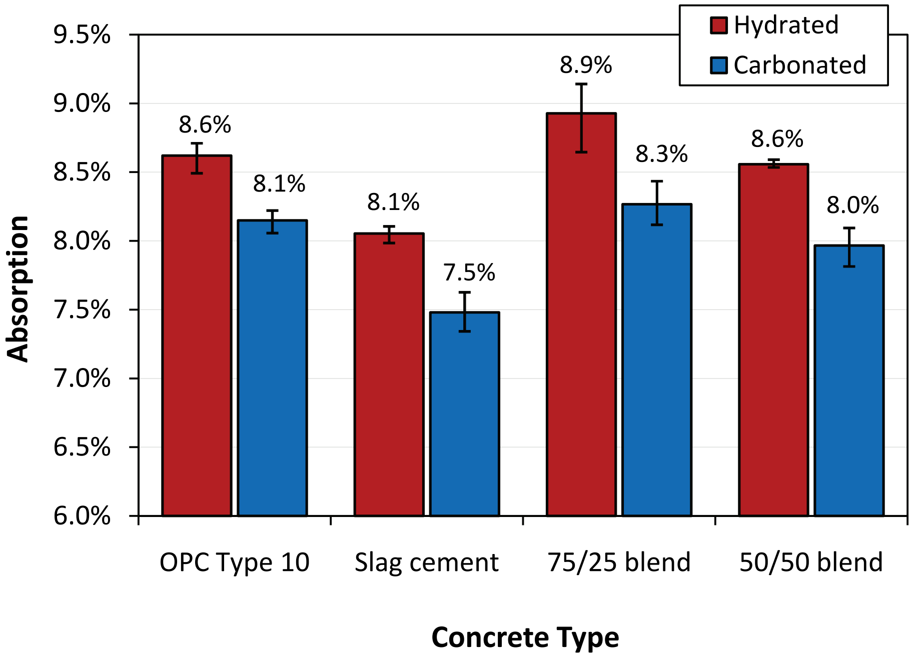

Figure 5.9: Comparison of the absorption of 28-day concretes subjected to either hydration or 2 hours of carbonation before hydration

Chapter 6

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INTEGRATION OF CARBON SEQUESTRATION INTO CURING PROCESS OF PRECAST CONCRETE

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Sean Monkman and Yixin Shao

PREFACE

The preceding research has demonstrated that it is possible to achieve the sequestration of carbon dioxide into concrete products through their curing, while improving the properties of the concrete. However, before the idea can be implemented, the merit and the scale of pursuing the scheme must be assessed. The use of carbonation-curing of concrete products as a greenhouse gas mitigation strategy requires consideration of the overall potential for reducing CO_2 emissions with the evaluation of any energy required to undertake the process so that a net benefit can be estimated. The amount of CO_2 that would be produced must be shown to be small in comparison to the amount that can be sequestered for the idea to be feasible.

The research presented in the following chapter assesses the feasibility of a carbonation-curing based sequestration strategy by estimating the energy requirements of proposed carbonation-curing approaches and determining the associated net carbon dioxide storage. The potential magnitude of carbon dioxide sequestration in concrete building materials is estimated by considering the market size of the appropriate concrete products and the established carbonation uptake in the various types of concrete. Some ideas for improving the uptake efficiency are presented.

Beyond straightforward sequestration considerations, the adoption of carbonation-curing as a way of accelerating the early age strength development of concrete would hinge upon how it compares with the existing methods of achieving the same goal, such as steam-curing or autoclaving. A comparison of the energy requirements for carbonation-curing with the energy requirements for these methods, presented here, is an integral part of the overall feasibility assessment.

The work is presented in the form in which it was submitted for review to the Canadian Journal of Civil Engineering.

ABSTRACT

The feasibility of integrating carbon sequestration into the curing of precast concrete products was investigated. The research program assessed the CO_2 uptake capacities of carbonation-cured concrete masonry units (CMU), concrete pavers, fibreglass mesh-reinforced cement board, cellulose fibre board and ladle slag fines. Three different curing systems were used: (1) an open-inlet system using pressurized recovered CO_2, (2) a closed system using pressurized flue gas with 14% CO_2, and (3) a closed system using dilute CO_2 under atmospheric pressure. The amount of carbon dioxide that could be sequestered in the annual North American output of the considered precast concrete products was estimated. The net efficiency was calculated accounting for CO_2 emissions penalty resulting from the capture, compression and potential transport of the curing gases. Carbonation-curing of the products considered could result in a net annual sequestration of about 1.8 million tonnes of carbon dioxide in US and Canada.

INTRODUCTION

Carbon sequestration has been identified as an important greenhouse gas mitigation strategy for addressing anthropogenic carbon dioxide emissions. Current approaches focus upon carbon capture and storage (CCS) in oceans, aquifers, and depleted gas and oil wells (IPCC 2005). Excluding the sites where CO_2 storage can be integrated into enhanced oil recovery (EOR) production, CCS typically has no economic benefit. One challenge currently facing carbon sequestration is to find beneficial uses of as-captured or recovered CO_2.

Carbon dioxide is a valuable industrial gas that is used in a variety of chemical processes. Approximately 110 million tonnes of carbon dioxide are used yearly as a raw material for the production of urea, methanol, acetic acid, polycarbonates and cyclic carbonates. The largest use is for urea production which reaches about 90 million tonnes. Except for polycarbonate production, which has a potential to consume 0.6 million tonnes of CO_2 per year, carbon dioxide stored in other chemical materials, including urea, has a limited lifetime and it will eventually escape to the atmosphere and then it needs to be captured again (IPCC 2005).

The carbonation reaction between carbon dioxide and appropriate calcium compounds results in a permanent fixation of carbon dioxide in a thermodynamically stable calcium carbonate. It was found that almost all calcium-carrying materials had the capacity to bind CO_2 into $CaCO_3$ (Johnson 2000; Monkman and Shao 2006). This carbonation process can be potentially integrated into the curing step of a precast concrete production and offer a beneficial use of the captured carbon dioxide. The potential of CO_2 uptake by precast concretes exposed to a carbon dioxide of 99% purity has been studied. It ranged from 9% to 16% by binder mass, depending on their compositions, with a corresponding reaction efficiency ranging from 18% to 32% (Shao et al. 2006).

Carbonation-curing of concrete offers technical benefits to the final products. The rapid strength gain by carbonation prompted research on its mechanism (Berger et al. 1972; Young et al. 1974). The technology was applied to the treatment of concrete blocks to reduce shrinkage by as much as 50% under subsequent exposure to carbon dioxide or to wet-dry cycles (Toennies 1960). The fast strength development contributed to the enhanced compatibility of wood particles with cement in the fabrication of wood-cement particle board (Hermawan et al. 2002; Soroushian et al. 2003). The permeability of carbonated concrete can be reduced due to the precipitation of calcium carbonate crystals (Venhuis and Reardon 2001) and efflorescence can be reduced by the deliberate reaction of calcium hydroxide. Despite of all of the technical benefits, there has been no large scale industrial implementation of the process, probably due to the cost of producing high purity carbon dioxide gas.

It is possible that this obstacle will be removed in the near future when, prompted by the development of large-scale CCS, carbon dioxide of high purity will become a by-product from hydrocarbon-based power generation or cement production. A system of carbon credits, or a carbon tax, can provide an incentive for concrete producers to consider carbon dioxide as their curing agent. The current trading value of carbon dioxide is between 4.00 and 40.84 USD per tonne in US, Canada and Europe (NETL 2008). It is hoped that a concrete curing process could offer a carbon sequestration approach that combines environmental, technical and economic benefits.

The purpose of this chapter is to identify commercially available precast products that are suited to carbonation treatment, estimate the amount of carbon that can be consumed by each product market and suggest how these processes could be integrated into existing production. The concrete curing processes are developed to be able to employ either relatively pure recovered CO_2 or an as-captured flue gas with a low concentration of CO_2. The concrete technology is potentially a sequestration methodology that can work directly with flue gas without separation. The processes will be evaluated based on carbon uptake and performance gain. The energy that is required for carbonation-curing is calculated and compared to the traditional steam curing and autoclave curing.

METHODOLOGY

Carbonation of Concrete Products

CO_2 uptake by carbonation-curing of precast concrete products depends upon the fabrication technology of the product and the amount of cement and water used. Different formulations have varying capacities to bind carbon dioxide and develop performance. It is best suited to those that presently employ steam curing or autoclave curing in their production but is also appropriate for others that are cured in air but may benefit from additional carbonation. The potential products include concrete masonry units (CMU), concrete paving stones, mesh reinforced cement boards, and cement bonded cellulose fiberboards. They are mass produced, require special curing treatments, and can realize several benefits through carbonation-curing.

The carbonation of very early age concrete is primarily the reaction of tricalcium silicate and dicalcium silicate in the cement binder with carbon dioxide to form thermodynamically stable calcium carbonates (Young et al. 1974). The challenge is to take advantage of this reaction in a time that is both sufficient to maximize the carbon dioxide uptake and advantageous for industrial production. A fundamental study was carried out to quantify the carbon sequestration potential for each candidate product. Three systems were considered. The first was an open-inlet system with pressurized recovered CO_2 of 99% purity. The second used a closed system with pressurized flue gas of 14% CO_2. The third approach considered the use of blended gas of 50% CO_2 at atmospheric pressure.

Open-inlet System Using Pressurized CO_2 of High Concentration

The open-inlet system consists of high purity recovered CO_2 introduced in a sealed chamber with the inlet gas valve left open to ensure a continuous supply of carbon dioxide. The experimental setup is shown in Figure 6.1. The precast products are placed into the chamber immediately after their formation with the curing gas injected up to a prescribed pressure. The continuous supply of CO_2 in the open-inlet system assures that any carbon dioxide that reacts with the concrete is immediately replaced by fresh CO_2 from the gas source. As a result, the gas pressure and CO_2 concentration remain constant throughout the process. The reaction time is selected based upon carbon uptake and performance gain. A reasonable time for recovered CO_2 is about two hours beyond which the reaction slows down and uptake efficiency is not improved (Shao et al. 2006). The pressure curve, reaction temperature, mass curve and CO_2 concentration are process parameters recorded in a data acquisition system to monitor the carbonation reaction. Laboratory testing with cement paste found that the pressure of the gas did not have a significant influence the reaction temperature (Figure 6.2) or the mass gain (Figure 6.3). The evidence suggests that, for the two gas pressures investigated (500 kPa and 150 kPa), the reaction degree and rate were not pressure dependent.

Closed System Using Pressurized Flue Gas of Low CO_2 Concentration

The closed system is appropriate for the direct use of as-captured flue gas without separation. The flue gas, containing 14% $CO_{2,}$ was collected from a cement kiln. To work with low concentration flue gas, a cyclic injection process was developed. An open-inlet approach would not work because the CO_2 concentration in the chamber would approach zero with time as the CO_2 absorbed by the concrete is replaced by dilute CO_2.

The flue gas was injected into the chamber (Figure 6.1) at a gauge pressure of 500 kPa. The chamber's inlet valve is then closed to permit the reaction to take place over a designated period of time. Since the system is closed, both the CO_2 concentration and the gas pressure in the chamber will be reduced as the concrete absorbs CO_2. Typical pressure and temperature curves of cement pastes cured with cyclic injection over time periods of 30-40 minutes are shown in Figure 6.4. The pressure drop in each period is indicative of the amount of CO_2 absorbed by the cement. The CO_2 concentration in the chamber is also monitored by an infrared based CO_2 meter; a summary of a test is shown in Figure 6.5. The CO_2 concentration in the chamber is lower than that in the flue gas because of the dilution with air in the chamber. In this laboratory scale test, the CO_2 content of the gas in the chamber, at release, is zero (implying that the concrete absorbed all of the flue gas CO_2) in the first four cycles and reduced to a low, but measurable, level in last three cycles (implying that the CO_2 absorption had slowed or ended). Therefore, the duration of each curing period can be determined by monitoring the CO_2 concentration. For each cycle, once the concentration reaches zero, or is near zero, the gas in the chamber is released and refilled to start a new cycle. The curing should be terminated when the pressure and concentration are seen to remain constant which would indicate that no further carbonation reaction is occurring. This can be considered a pseudo-dynamic system with the flue gas having a measureable residence time in the chamber. The gas pressure and time period of each cycle should be determined by the scale of production. In this process, carbon capture and sequestration are effectively combined into a single step with useful concrete products serving as the sequestration medium.

Using Blended Gas at Atmospheric Pressure

The use of flue gas without compression would be the best approach for minimizing the energy consumed preparing the gas. It is not likely to be suitable for curing precast products because such a gas would require an unacceptably long time to reach a certain degree of carbonation due to the low CO_2 content in the system. However, if longer exposure duration is permitted, the process can be appropriate for sequestration. The longer carbonation times of this type of approach would be suitable for a place where calcium rich materials are produced alongside carbon dioxide point sources, such as steel slag at a steel plant. Steel slag could be carbonated by exposing it to flue gas as it is being vented. Passing flue gas through slag would effectively remove carbon dioxide from the gas in the manner of a flow-through reactor. The approach would be relatively straightforward and the kinetics of the carbonation reaction would likely benefit from the higher gas temperature.

The carbonation treatment of steel slag was simulated in the lab at ambient pressure and temperature under a relative humidity of 65%. A blended gas of 50% CO_2 and 50% air was used to accelerate the test but this is analogous to dilute CO_2 in flue gas. The gas was introduced into the chamber and the chamber was closed. The chamber was vented and refilled periodically as the samples were assessed.

Quantification of CO_2 Uptake

The CO_2 contents of the carbonated products were by the change in mass of the sample before and after carbonation. CO_2 uptake estimated by mass gain (Equation 1) is determined by considering the initial mass, the final carbonated mass (including the lost water) and the original mass of the dry binder:

$$Mass\ gain\,(\%) = \frac{\left(Mass_{final} + Mass_{water\ loss}\right) - Mass_{initial}}{Mass_{dry\ binder}} = \frac{\Delta Mass_{CO_2}}{Mass_{dry\ binder}} \tag{1}$$

The water that evaporated and then condensed on the wall of the chamber due to the exothermic temperature rise was collected by absorbent paper and added to the final mass. For concrete products, the dry binder refers to the cement; for slag carbonation, it is the mass of slag. The mass gain method is simple, average-based and insensitive to sampling error. A detailed description of the method and comparison with infrared analysis has been given elsewhere (Shao, et al 2006).

RESULTS

Sequestration Potential of Concrete Products

This work considers the carbonation, using either recovered CO_2 or flue gas, of four widely used building products – concrete masonry units, concrete pavers, cement mesh board and fiber cement board. One industry waste, ladle slag, was also carbonated for use as a sand replacement in precast products. Appropriate lab tests were performed on samples analogous to commercial precast production. The CO_2 uptake was quantified as the mass gain. Estimates about the annual potential sequestration in US and Canada are summarized in Table 6.1 and the daily sequestration that could occur at a single production location is presented in Table 6.2. Detailed discussion is given as follows.

Carbon Uptake by Concrete Masonry Units

Concrete masonry units (CMU) are ideal candidate products for CO_2 sequestration. They are porous and are cured in a closed chamber with either low pressure or high pressure steam. The North American market for CMUs is predicted to increase to 4.3 billion units in 2010 (Freedonia Group 2006). An estimate of total CO_2 absorption can be made for the open-inlet system with recovered CO_2 and the closed system with flue gas.

The laboratory study was conducted to estimate CO_2 uptake by masonry units using a mix design that approximated industry formulations with a cement content of 10%, and a water to cement ratio of 0.26. The samples were compact formed with a pressure of 10 MPa and had dimensions of 76 × 127 × 25 mm. The fresh samples were placed in the curing chamber immediately after being formed and were subjected to one of two different curing schemes. In an open-inlet system curing (Figure 6.1) with recovered $CO_{2,}$ the process lasted two hours with constant pressure and CO_2 concentration. The absorption of carbon dioxide, by mass of cement binder, was 9.8%. The strength after two hours carbonation reached 78% of 24-hour hydration strength and was 440% of the two-hour hydration strength. In the closed system with as-captured flue gas, a multiple-injection approach used 7 cycles over a total of 5 hours. The absorption of carbon dioxide, by mass of cement binder, was 6.3%. The corresponding 5-hour carbonation strength was 4 times higher than the hydration reference. Although the carbon uptake is less in flue gas carbonation, the 5-hour flue gas carbonation strength was very close to that of 2-hour high purity gas treatment.

An estimation of the sequestration potential by CMU production is possible. If the 4.3 billion blocks produced are considered as standard 200-mm CMUs each containing 1.36 kg of cement, then the total amount of cement used per year would be about 5.9 million tonnes. The total amount of CO_2 stored through carbonation-curing could be 578 200 tonnes with recovered CO_2 (at an uptake rate of 9.8% by mass of binder), and would approximately 371 700 tonnes using flue gas (at an uptake rate of 6.3%).

For one CMU production site using one 6-block-at-a-time production machine that produces 3 240 units per hour, the total daily use (12 hours) of cement could be approximately 52.9 tonnes. Carbonation-curing using recovered CO_2 would consume 5.2 tonnes of CO_2 per day while using flue gas would consume 3.3 tonnes of CO_2 per day.

Carbon Uptake by Concrete Paving Stones

Interlocking concrete paving stones, including veneer stones, are high value products in the construction market. These products are used for walkways, driveways and building veneers. The paving stone products usually contain about 20% cement content with a density of 2200 kg/m^3 and a thickness range of 60-100 mm. Due to the high cement content and the high pressure forming process, paving stones are typically not subjected to any special curing scheme. Instead they are stacked on shelves, stored in rooms and cured by self-generated hydration heat. If the curing rooms can be sealed, then a carbonation treatment can be applied and provide additional technical benefits. In addition to the accelerated strength gain, carbonation does not form calcium hydroxide and leads to significantly reduced efflorescence. The latter effect is crucial for paving stones to ensure that they maintain their desired color while in service.

The annual North America production of pavers exceeds 74 × 10^6 square metres (800 million square feet (ICPI 2007)). Assuming an average thickness of 80 mm, a density of 2200 kg/m^3, and a cement content of about 20%, about 2.6 million tonnes of cement are used in the annual North American production of pavers. Assuming the same uptake rates as the CMU products, carbonation-curing of the pavers with recovered CO_2 would bind about 254 800 tonnes of carbon dioxide while the use of flue gas would bind about 163 800 tonnes in a year.

Paving stones are manufactured by similar block machines that make CMU but use different mix designs. If a typical machine can produce the same mass of pavers per day (over a 12 hour period) as the mass of CMUs that can be produced, then the total cement usage would be 105.8 tonnes. If all pavers are treated with carbon dioxide and the uptake rate is the same as CMU product, then the absorption will be 10.4 tonnes per day using recovered CO_2 and will be 6.7 tonnes per day using flue gas.

Carbon Uptake by Fiberglass Mesh Reinforced Cement Board

Fiberglass cement backboard consists of an aggregated cement based core matrix, reinforced with glass fiber scrims embedded on both sides of the board. Its primary use is the tile backboard. The board has a density range of 1200-1280 kg/m^3 and a typical thickness of 12.7 mm. It contains 40-60% cement by mass and uses a water to cement ratio of 0.35. Industry production incorporates curing in the form of either moist air curing, high pressure steam curing or chemically accelerated hydration. Carbonation-curing is ideal for this category of product because the large surface area to volume ratio will allow for an efficient reaction. More importantly, carbonation treatment can reduce the pH value of the cement matrix, protect glass meshes from alkali attack and lead to more durable products (Bentur and Mindess 1990).

The CO_2 uptake by mesh reinforced cement board was investigated in the lab (Wang 2007). The mixture had a water to cement ratio of 0.35 and a cement content of 70%. Mesh-cement samples, 12-mm thick, were formed by conventional casting to simulate the commercial cement board production. To facilitate carbonation, the board was conditioned to remove surface moisture by applying hot air to the board for about 20-30 minutes. The conditioned boards were then carbonated in two systems. Two hour carbonation in the open-inlet system with recovered CO_2 yielded a CO_2 absorption of 12.2% based on cement mass, while the five hour flue gas carbonation with 7 cycles gave an uptake of only 4.4%.

It is estimated that the production capacity of mesh cement board in US and Canada is approximately 75 million m^2/year (Venta 2000). If formulations can be assumed to have a thickness of 12.7 mm, a density of 1250 kg/m^3, and a cement content of about 50%, then about 595 000 tonnes of cement is consumed in the annual mesh board production. If all boards are treated by carbonation-curing, the corresponding CO_2 uptake will be 72 590 tonnes per year with recovered gas and 26 180 tonnes per year with flue gas. A single plant producing 9 570 m^2/day would use 76 tonnes of cement. The estimated carbon dioxide uptake when curing with recovered CO_2 would be 9.3 tonnes or 3.3 tonnes with flue gas.

Carbon Uptake by Cellulose Fibre Board

Cellulose fiber boards have been developed to replace asbestos cement and have become well accepted and used in the North America construction market. The typical thickness is 8 mm and typical density is 1300 kg/m^3. The production follows the traditional Hatschek (slurry-dewatering) process. Typical fiber cement consists of 52% cement, 32% sand, and 8% pulp. The board is formed by slip casting, dewatering, laminating and compact forming. The fiber cement is then pre-cured for 8 hours at 98% humidity and 60 °C, prior to autoclaving for 12 hours in saturated stream at 900 kPa and 176 °C. Since cellulose fiberboard requires both pre-curing and autoclave curing, this process could be possibly replaced by carbonation-curing to provide both accelerated hydration and carbon sequestration. Carbonation can also provide some technical advantages such as reducing the pH of the cement matrix which would serve to protect the cellulose fibers from alkali attack and thus inhibit the aging process.

Laboratory work was carried out (Wang 2007) to quantify the CO_2 absorption capacity in cellulose fiberboard. Specimens were press formed with a pressure of 0.7 MPa to form a 76 × 127 × 13 mm sample. The moulded specimens were then pre-cured at 60 °C for about 30 minutes and were subjected to carbonation using two systems.

For the recovered gas and a fiberboard with 12% fibers, two hours of carbonation using the open-inlet system achieved a CO_2 uptake of 18.9%. The 2-hour modulus of rupture (MOR) reached 4.1 MPa, which doubled the 8-hour hydration MOR of a reference. The corresponding two-hour compressive strength by carbonation was 10.5 MPa which more than tripled the eight-hour hydration strength of 3.1 MPa. For flue gas carbonation using a closed system with 11 cycles in 8 hours, the CO_2 uptake was 8.1% by cement mass. The corresponding 8-hour strength was 3.8 MPa in bending and 6.9 MPa in compression, both of which were about double the hydration reference at same age. It is likely that the lower carbon uptake and lower strength gain are attributable to the lower partial pressure of the carbon dioxide in the flue gas.

The annual North American fiber cement production is about 910 million m^2/year (9.8 billion sf/yr (James Hardie 2008)). Assuming a typical thickness of about 8 mm (5/16“), a density of 1500 kg/m^3 and a cement content of 48%, the annual production represents the consumption of approximately 4.8 million tonnes of cement. If the total fiber cement production was carbonation-cured, the annual carbon dioxide storage in fiber cement could reach 907 200 tonnes using recovered CO_2 and 388 800 tonnes using flue gas. For one fibre cement plant with a capacity of 28 million m^2/yr (300 million ft^2/yr), the daily fibre cement production would be 76 359 m^2 with a cement requirement of about 400 tonnes. If the production is carbonation-cured, then the daily uptake at one plant would be 75.6 tonnes using recovered CO_2 or 32.4 tonnes using flue gas.

Carbon Uptake by Ladle Slag Fines as Sand Replacement

Ladle slag was studied to determine the capacity for carbon uptake and the possibility of using it as a sand substitute (Monkman, et al 2008)[1]. A laboratory trial used a ladle slag (58% by weight CaO by XRF analysis) that was a fine powder in the as-received condition. About 90% of the particles were smaller than 600 microns in size and the slag would not necessarily need crushing or grinding. The slag was carbonated with a dilute CO_2 (50%) at atmospheric pressure. The carbonation treatment significantly reduced the free lime content of the slag and showed a carbonation uptake that varied by particle size. The smallest particle size, <75 µm, had an uptake of 12.7% after 56 days of atmospheric carbonation. The largest particle size, 300-600 µm, had an uptake of 4.2%. The carbonation uptake of the as–received and ungraded slag was 10.8%.

The performance of carbonated slag sand was compared to that of reference river sand in a concrete with a water to cement ratio of 0.20, sand to cement ratio of 2, and dimensions of 76 × 127 × 15 mm formed under a compaction pressure of 8 MPa. Table 6.3 summarises the test results. Concrete samples with the carbonated ladle slag sand were shown to have the same hydration strength as samples made with river sand after 28 days indicating that the carbonated

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[1] Monkman, S., Shao, Y., and Shi, C. J. 2009. Carbonated Ladle Slag Fines for Carbon Uptake and Sand Substitute. Accepted for publication by the ASCE Journal of Materials in Civil Engineering.

slag could be considered as a river sand substitute. When such concretes were initially carbonation-cured for two hours in an open-inlet system before being hydrated for 28 days, the slag sand concrete had a strength that was 25% lower. However, in terms of the total carbon dioxide sequestration (Table 6.3) the total amount of carbon dioxide was 24.2% (by mass of binder) in the carbonated concrete containing the carbonated slag sand. The use of carbonated ladle slag as a sand in the concrete products considered could double their sequestration potential.

The annual North America production of ladle slag is not reported but is estimated to be on the order of 1 to 2 million tonnes per year. The carbonation of 2 million tonnes of this slag, at an uptake of 10.8%, could absorb 216, 000 tonnes of carbon dioxide producing 2.2 million tonnes of manufactured sand for use in other concrete products. While this amount is potentially modest, there are a variety of other calcium-rich slags that might be employed similarly.

ENERGY AND CO_2 PENALTY ANALYSIS

The three main steps, recovery, compression and transportation, involved in carbonation-curing will each have their own energy requirements and CO_2 penalties. This work estimates the carbon dioxide emissions associated with the preparation of one tonne of high purity CO_2, to calculate a net sequestration efficiency related to a tonne of CO_2 absorbed into concrete products.

Energy Requirements for Using Recovered CO_2

Recovered CO_2 of high concentration provides the highest reaction efficiency for carbonation-curing but to integrate it into concrete production requires additional energy. High purity carbon dioxide would be extracted from flue gas and then compressed to the desired pressure. Extensive research has been conducted on CO_2 capture using different separation techniques. The electrical energy required for post-combustion capture of CO_2 from a typical flue gas stream using an alkanolamine solvent is estimated to be about 198 kWh/tonne CO_2 (Feron 2005). This consists of 178 kWh/tonne for the thermal requirements for solvent regeneration and 20 kWh/tonne for the additional electricity required in the capture process. The emission factor per kWh of electrical energy produced can be taken to be about 605 g of CO_2 in the United States (Electrical power production in the United States in 2006 totalled 4,064,702 GWh with associated CO_2 emissions of 2,459,800 MT, Energy Information Administration 2007) and 220 g in Canada (Environment Canada 2007). (About 71% of the electricity generated in the United States comes from fossil fuel combustion. Canada meets a higher proportion of its energy needs by nuclear and hydroelectric sources meaning that fossil fuel combustion is only responsible for about 25% of its electricity production.) Thus, the current energy required to recover one tonne of CO_2 will itself typically result in a CO_2 penalty of 119.8 kg using the American emissions factor or 43.6 kg using the Canadian emissions factor.

Once the CO_2 has been recovered, it needs to be liquefied for either transport off site or storage on site. CO_2 transported by tanker is compressed and liquefied to 2 MPa and -31 °C (IPCC 2005) and can be stored under these conditions. The energy required to compress the gas from atmospheric to 2 MPa in a two stage compression (assuming 85% compressor efficiency, an intercooling pressure drop of 25 kPa, and no energy required for cooling to atmospheric temperature) was calculated using thermodynamics data from the National Institute of Standards and Technology (NIST 2005). The compression ratio, along with the specific heats of the gas, was used to determine the final gas temperature. The pressure at the end of the stage and the gas temperature were used to determine the thermodynamic data. The energy for adiabatic compression, 73.4 kWh/t, was the sum of the energy required for the two stages (36.1 and 37.1 kWh/t). The liquefaction of the CO_2 (isobaric cooling of the gas from 25 °C to -31 °C) requires an additional 19.1 kWh/t. The total energy requirement would be 92.5 kWh/tonne. The calculation is summarised in Table 6.4. The electrical energy required to compress one tonne of CO_2 to 2 MPa for low pressure storage or transport would result in the emissions of 56.0 kg of CO_2 (20.4 kg in Canada). It is calculated that the recovery energy, representing over 60% of the emissions total, is dominant.

An industry standard vacuum insulated cryogenic storage container can hold upwards of 60 tonnes of liquid CO_2 without the need for additional refrigeration (provided the CO_2 is subject to regular withdrawal, as it would be in a carbonation-curing scheme) (ASCO Carbon Dioxide Ltd 2008). A vaporizer would be required to change the liquid CO_2 to a gas at 150 kPa and atmospheric temperature. A vaporizer that can process a tonne of CO_2 in an hour would consume 2.76 kWh (ASCO Carbon Dioxide Ltd 2008) with an associated CO_2 penalty of 1.7 kg (or 0.6 kg in Canada). The total CO_2 penalty related to preparing recovered CO_2 is then the sum of the recovery, compression and vaporization steps and is 177.4 kg CO_2 in the United States and 64.5 kg in Canada. As shown in Table 6.5, the net sequestration efficiency would then be 82.3% in the United States or 93.5% using Canadian emissions factors.

It is likely that the recovered CO_2 would have to be transported to a distant location for use in carbonation-curing. The four main options for transport of CO_2 would be pipeline, ship (marine), rail tanker, or road tanker. Each of these cases involves energy for compressing the gas prior to transport and CO_2 penalties related to the transportation method itself. Since most precast concrete plants are currently accessible only by roads, the dominant mode of transporting CO_2 would be by tanker truck. Additionally, precast concrete plants are typically within 50-100 km of a cement plant. Therefore, cement kiln flue gas can be an ideal source of CO_2 for concrete plant.

Road transport, in a 20 tonne diesel truck, can be taken to emit carbon dioxide at 71.4 g CO_2/tonne·km (Kawai et al. 2005). A typical liquid CO_2 shipping container does not require additional refrigeration. Additionally, a typical container that transports 20.0 tonnes of liquid CO_2 would have a container weight of about 10.6 tonnes meaning that the liquid can be assumed to represent 65% of the transported tonnage (ASCO Carbon Dioxide Ltd 2008). Transportation of a tonne of CO_2 150 km by road would result in an emission of 16.4 kg of CO_2. The total emission, including recovery, compression and vaporization, would be 193.8 kg (80.9 kg in Canada). The net sequestration efficiency would be 80.6% in the United States and 91.9% in Canada. The result is summarized in Table 6.5 as the off site option.

Energy Requirements for Using Flue Gas

The use of flue gas must consider the compression energy on the basis of the CO_2 in the gas since that is part of the gas mixture that will take part in the carbonation reaction. Such a consideration makes it apparent that the use of flue gas for carbonation-curing is logical only in the immediate vicinity of a flue gas point source so that transportation (and the required compression) is relatively minor factor. The compression of one tonne of CO_2 in flue gas to pressures between 150 and 500 kPa is summarised in Table 6.6 (the data was calculated in the same manner as with compression of recovered CO_2).

The sequestration efficiency of one tonne equivalent of CO_2 in compressed flue gas would exceed the net sequestration efficiency offered by recovered CO_2 compressed for on site storage (which would be 82.3% in the United States, 93.5% in Canada and is shown in Table

6.5) at pressures lower than 400 kPa (Table 6.6). Transportation of flue gas would require compression to much higher pressures and increase the associated emissions to an unfavourable level. However, the operational cost and the system complexity could be much less with the direct use of flue gas.

Comparison with Steam-curing and Autoclave-curing

Steam curing and autoclave curing are well established processes in precast concrete industry for accelerated production. For one cubic meter of concrete, steam-curing requires 0.593 GJ/m^3 of concrete while autoclave curing requires 0.712 GJ/m^3 of concrete (Kawai et al. 2005). The emissions associated with steam-curing are 38.5 kg CO_2 emitted/m^3 and for autoclave-curing it is 46.2 kg CO_2 emitted/m^3. When considering concrete masonry units, one cubic metre of concrete, at 2200 kg/m^3 and 10% cement, would contain about 220 kg of cement. Curing one cubic meter concrete with recovered CO_2, at an uptake of 9.8%, would need 21.6 kg of CO_2. If carbonation is carried out at the site of recovery and at 150 kPa pressure, the corresponding CO_2 penalty, based on Table 6.5, would be 177.4 kg/t CO_2, or 3.8 kg CO_2 emitted/m^3. The carbonation-curing emissions would only be 9.9% of those associated with steam-curing and only 8.3% of what is associated with autoclaving (1.4 kg of emissions, 3.6% of steam-curing and 3.0% of autoclaving using Canadian emissions factors). Since the CO_2 penalty is calculated based on the energy consumption, carbonation requires much less energy than steaming and autoclaving.

Implementation, Economics and Challenge

Carbonation-curing of the North American output of the considered products could result in the sequestration of 2.029 million tonnes of carbon dioxide when using recovered CO_2 and 1.166 million tonnes when using flue gas. If this storage was considered at a typical net sequestration efficiency of 87.1% for recovered CO_2 (an average of the four considered cases) and 84.0% for flue gas (an average of the two cases of flue gas compressed to 500 kPa) then the net sequestration would be 1.767 million tonnes using recovered CO_2 and 979 668 tonnes using flue gas.

The ideal implementation for this approach would involve the placement of production lines nearest the point sources of CO_2. This would eliminate the time, costs and risks of transporting the carbon dioxide. Integration of carbonation-curing into established concrete production would require the transportation of carbon dioxide because the precast producers are strategically distributed based upon the market demands and not necessarily adjacent to major CO_2 sources. The transportation requirement of CO_2 for carbonation-curing is not any different from the transportation required for CO_2 capture and storage in geological formations. Thus, in terms of carbonation-curing being a sequestration initiative, the transport of CO_2 would not be considered a barrier to adoption or otherwise hamper the development of the concept.

The cost, including separation and compression, of recovering CO_2 from flue gas is about \$32 to \$54 per tonne (Feron 2005). If the trading value of carbon dioxide was taken to be \$40 per tonne then use of recovered CO_2 for this carbon storage method would be economically attractive. The cost of using flue gas could be offset by the value of the carbon credit (if the energy for compressing flue gas to 500 kPa, 388.2 kWh, is converted at a rate of 10 ¢/kWh).

Additionally, either approach would offer direct energy savings if carbonation replaces steam curing or autoclaving.

The use of flue gas would eliminate the cost associated with recovering the CO_2 and be a viable approach for on-site treatment. It is particularly suited to treating calcium-rich steel slag wastes that are often produced alongside CO_2 rich flue gas and often sent to landfills. The carbonation of steel slag with flue gas at atmospheric pressure could proceed with almost no energy consumption and provide a material that can be used as a sand substitute in concrete to enhance carbon uptake and preserve natural resources. The challenge of using pressurized flue gas in a curing process is the compression energy at high gas pressure. A dynamic flow system could possibly provide a solution to the problem of supplying sufficient flue gas CO_2 at low pressure.

It is suggested that technological advancement can feasibly reduce the energy associated with carbon capture from 198 kWh/t to 93 kWh/t (Feron 2005) within a decade. This represents that largest energy input into the recovered CO_2 approach. The operational costs might be reduced in the near future if high purity carbon dioxide would be widely available. Dedicated CO_2 recovery efforts may not be necessary if CO_2 is being widely recovered as part of power generation. The transportation costs would then be the most significant emissions aspect to consider for acquiring CO_2 for carbonation-curing. Alternatively, if the cement industry moves to use carbon capture and storage as a way of addressing the CO_2 emissions then opportunities would exist for co-operation between the clinker producers and precast producers. If the CO_2 emissions intensity for a tonne of cement is about 670 kg/tonne produced (World Business Council for Sustainable Development 2008) and that tonne of cement can be carbonation-cured at a mass gain of about 12% then the specific emissions intensity would essentially be reduced by almost 18% to 550 kg/tonne of cement.

Beyond the probable costs of the carbon dioxide acquisition or preparation, the approach would offer some distinct benefits for concrete production. The total energy consumed in carbonation-curing is much less than that required by steam-curing and autoclave-curing. Moreover, the accelerated production potentially provided by carbonation-curing might be considered a way of reducing manufacturing costs while the increased durability of the products can be seen as a way of adding value.

CONCLUSIONS

The proposed process offers a feasible method of safe and permanent sequestration of carbon dioxide in manufactured concrete products. Either recovered carbon dioxide or flue gas could be used. The preparation of the recovered $CO_{2,}$ including energy for recovery and liquefaction to a storage pressure of 2 MPa results in a net sequestration efficiency of about 82.3% (93.5% using Canadian emissions factors). Transport of the liquid CO_2 150 km by truck would result in a net sequestration efficiency of 80.6% (91.9% in Canada). Although the direct use of flue gas can save considerable energy and the costs associated with the CO_2 separation and recovery process, the reaction efficiency is lower since there is only a fraction of carbon dioxide available for reaction at a given pressure. Flue gas contains CO_2 in a dilute form and transportation of flue gas would be unfavourable. The direct use of flue gas as a carbonation-curing agent is only appropriate for situations in which the curing is performed adjacent to the point source and can be competitive, on the basis of a tonne of CO_2 stored, to recovered CO_2 if the process is carried out at a gas pressure below 400 kPa.

Commonly used precast concrete building products such as masonry units, paving stones, cement boards and fibreboards are ideal candidates for CO_2 storage. In the United States and Canada, the cement consumed in their production is about 14 million tonnes. If all of these products were carbonation-cured then the net annual sequestration of CO_2 would reach 0.98 million tonnes using flue gas (at a net efficiency of 84.0%) or 1.8 million tonnes of CO_2 using recovered CO_2 (at a net efficiency of 87.1%). With a low energy consumption and high gain in performance, carbonation-curing technology offers a promising tool in greenhouse gas control.

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TABLES

Table 6.1: Annual sequestration potential by concrete products in United States and Canada

	CMU	Paver	Mesh board	Fiberboard	Ladle slag
Annual production	4.3×10^9 units	74×10^6 m^2	75×10^6 m^2	9.1×10^8 m^2	2×10^6 tonnes
Cement used in product (Mt)	5.9	2.6	0.595	4.8	-
Uptake from recovered CO_2 (Mt)	0.578	0.255	0.073	0.907	-
Uptake from flue gas (Mt)	0.372	0.164	0.026	0.389	0.216

Table 6.2: Amount of carbon dioxide required by daily production for carbonation-curing

	CMU	Paver	Mesh board	Fiberboard
Capacity per line	38 880 units/day	5 420 m^2/day	9 570 m^2/day	76 359 m^2/day
Thickness (mm)	200	60-100	13	8
Cement content (wt%)	10	20	50	48
Cement consumed (t)	52.9	105.8	76.0	400
Uptake with Recovered CO_2	9.8%	9.8%	12.2%	18.9%
Recovered CO_2 needed for a day (t)	5.2	10.4	9.3	75.6
Uptake with flue gas CO_2	6.3%	6.3%	4.4%	8.1%
Flue gas CO_2 needed for a day (t)	3.3	6.7	3.3	32.4
Flue gas (14% CO_2) needed per day (t)	23.8	47.6	23.9	231.5

Table 6.3: Summary of carbon dioxide sequestration in slag sand concrete

	River sand concrete		Slag sand concrete	
	28 d hydration	2 hr carbonation + 28 d hydration	28 d hydration	2 hr carbonation + 28 d hydration
Total dry mass (g)	822.3	822.2	721.0	723.4
Cement mass (g)	274.1	274.1	240.3	241.1
Sand mass (g)	548.2	548.1	480.7	482.3
Mass of CO_2 in sand (g)	0	0	23.3	23.5
Mass of CO_2 in cement (g)	0	34.9	0	34.8
Total CO_2 (g)	0	34.9	23.3	58.3
% CO_2 by total dry mass	0.0%	4.2%	3.2%	8.1%
% CO_2 by cement mass	0.0%	12.7%	9.7%	24.2%
Strength (MPa)	17.9	20.9	17.4	15.5

Table 6.4: Estimated energy for compression of recovered CO_2 to 2 MPa and -31 °C

		Step				
		1	2	3	4	5
		Compress	Cool	Compress	Cool	Liquefy
T_0	°C	25	148.5	25	148.5	25
P_0	kPa	101.3	465.6	440.6	2025.0	2000.0
h_0	kJ/kg	505.8	-	502.6	-	486.5
s_0	kJ/kg·K	-	-	-	-	2.127
Compression ratio	-	4.60	-	4.60	-	-
Pressure Drop	kPa	-	25	-	25	-
T_1	°C	148.5	25.0	156.2	25.0	-31.0
P_1	kPa	465.6	440.6	2025.0	2000.0	2000.0
h_1	kJ/kg	616.2	-	616.8	-	131.3
s_1	kJ/kg·K	-	-	-	-	0.739
Δh	kJ/kg	110.4	-	114.2	-	-355.2
Δs	kJ/kg·K	0	-	0	-	-1.388
$T_0\Delta s$	kJ/kg	0	-	0	-	-413.7
ΔG	kJ/kg	110.4	-	114.2	-	58.6
Energy	kWh/t	30.7	-	31.7	-	16.3
Final Energy	kWh/t	36.1	-	37.3	-	19.1

Note: h= enthalpy, s = entropy, G = Gibbs free energy = $\Delta h - T_0\Delta s$. Compression assumed to be adiabatic with an intercooling pressure drop of 25 kPa, isobaric cooling assumed from 25 °C to -31 °C. Final energy reflects a compressor and liquefaction efficiency of 85%.

Table 6.5: Estimated energy and CO_2 penalty (CO_{2e}) for on site or off site recovered CO_2 curing

			On site		Off site	
Step	Aspect	Unit	US	CAN	US	CAN
Recovery	Energy	(kWh/t)	198	198	198	198
	CO_{2e}	(kg/t)	119.8	43.6	119.8	43.6
Compression	Pressure	(MPa)	2	2	2	2
	Energy Required	(kWh/t)	92.5	92.5	92.5	92.5
	CO_{2e}	(kg/t)	56.0	20.4	56.0	20.4
Transport	distance	(km)	-	-	150	150
	CO_{2e}	(kg/t)	-	-	16.4	16.4
Vaporizer	Energy Required	(kWh/t)	2.8	2.8	2.8	2.8
	CO_{2e}	(kg/t)	1.7	0.6	1.7	0.6
Total	CO_{2e}	(kg/t)	177.4	64.5	193.8	80.9
	Net Efficiency	(%)	82.3	93.5	80.6	91.9

Note: CO_2 emissions due to energy consumption are calculated at a rate of 605 g/kWh in the United States, 220 g/kWh in Canada. Emissions due to truck transport are taken to be 71.4 g/tonne·km with the CO_2 representing 65% of the gross weight shipped.

Table 6.6: Estimated energy and CO_2 penalty (CO_{2e}) for on site flue gas curing

Pressure (kPa)	150	200	300	400	500
Energy Required (kWh/t of gas)	11.3	20.4	34.7	47.4	54.4
Energy Required (kWh/t of CO_2)	80.7	145.8	247.8	338.7	388.2
US CO_{2e} penalty (kg)	48.8	88.3	149.9	204.9	234.9
CAN CO_{2e} penalty (kg)	17.8	32.1	54.5	74.5	85.4
US Net Efficiency (%)	95.1%	91.2%	85.0%	79.5%	76.5%
CAN Net Efficiency (%)	98.2%	96.8%	94.5%	92.5%	91.5%

Note: Compression energy calculated assuming adiabatic compression at an efficiency of 85%, with dry flue gas containing 75.6% N_2, 14.0% CO_2, and 10.4% O_2. Gas cooled to 25 °C before compression. Calculated at a one stage compression up to 300 kPa and two-stage compression at higher pressures. The CO_2 emissions due to energy consumption are at an assumed rate of 605 g/kWh in the United States, 220 g/kWh in Canada.

FIGURES

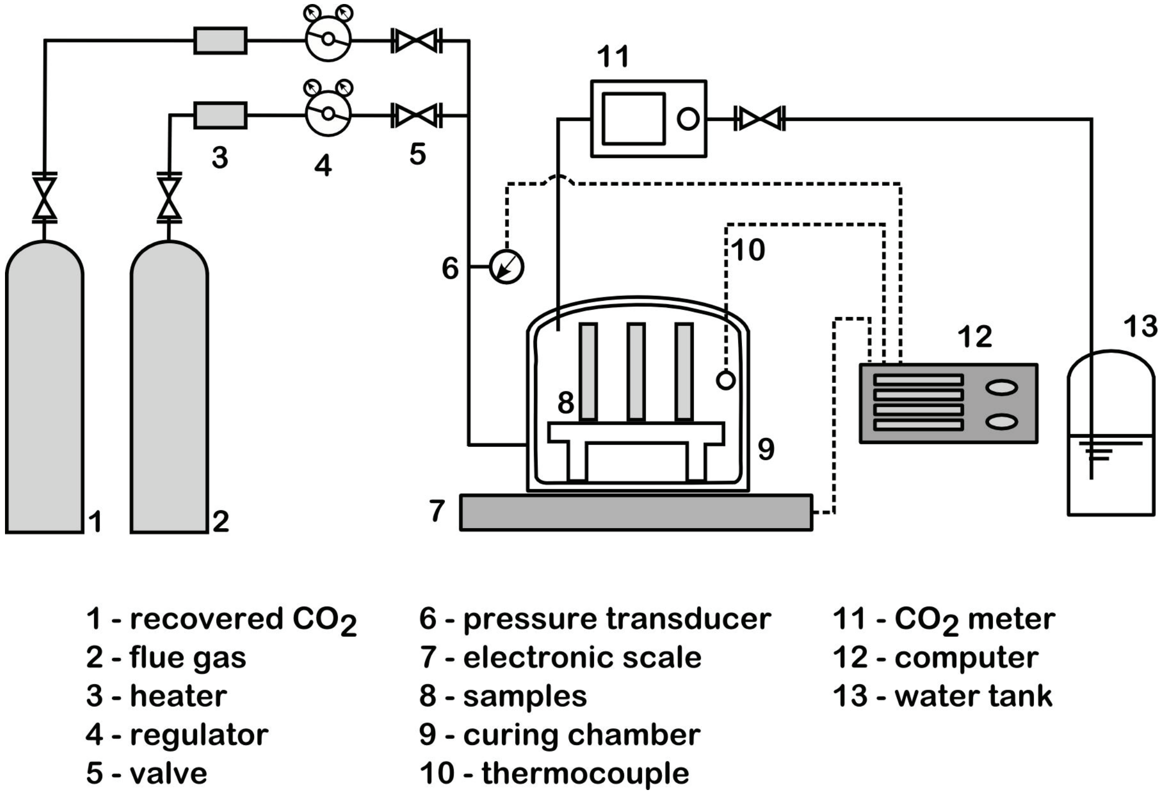

Figure 6.1: Carbonation-curing schematic for using either pressurized recovered CO_2 or pressurized flue gas

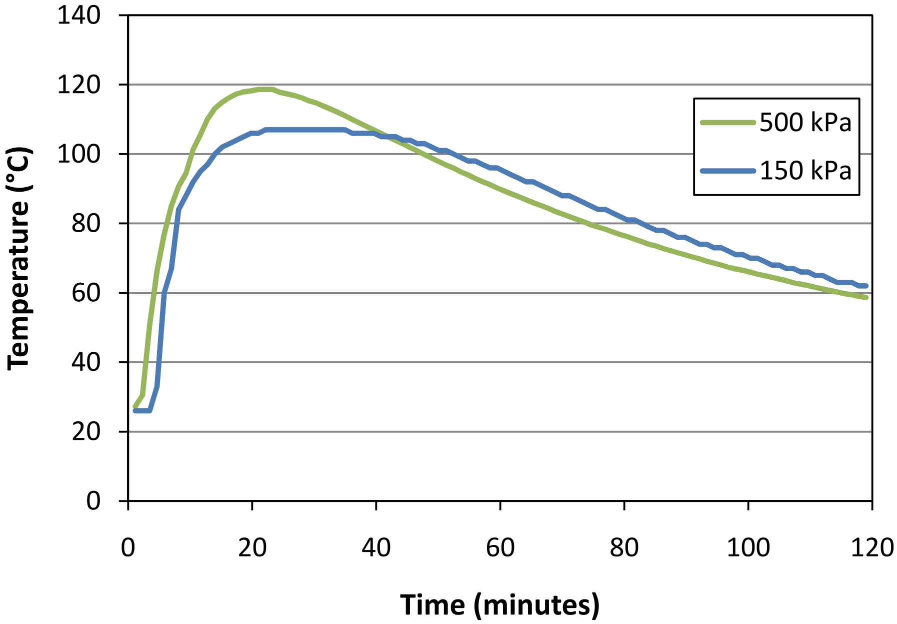

Figure 6.2: Effect of gas pressure on carbonation reaction temperature of cement paste exposed to recovered CO_2

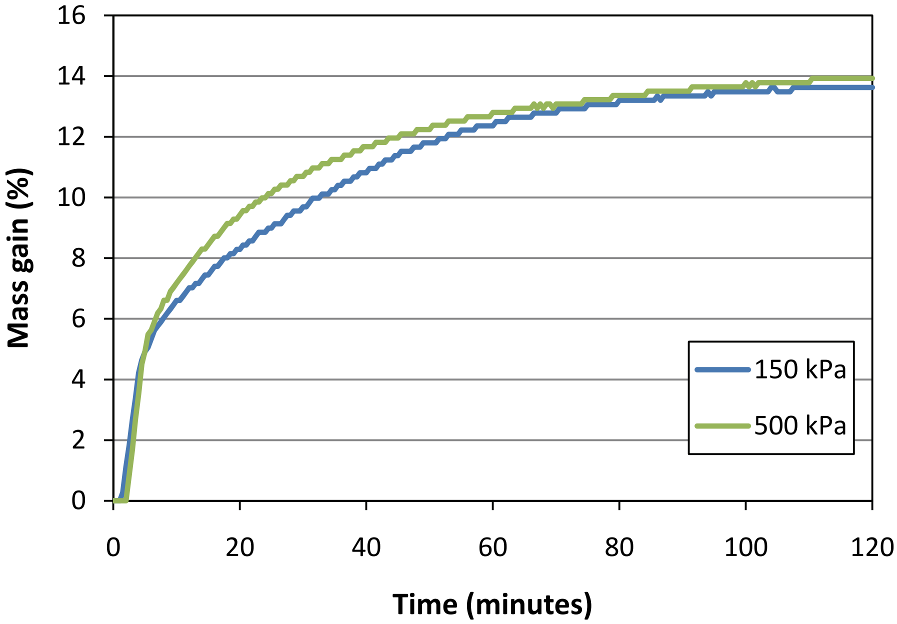

Figure 6.3: Effect of gas pressure on CO_2 mass uptake of cement paste exposed to recovered CO_2

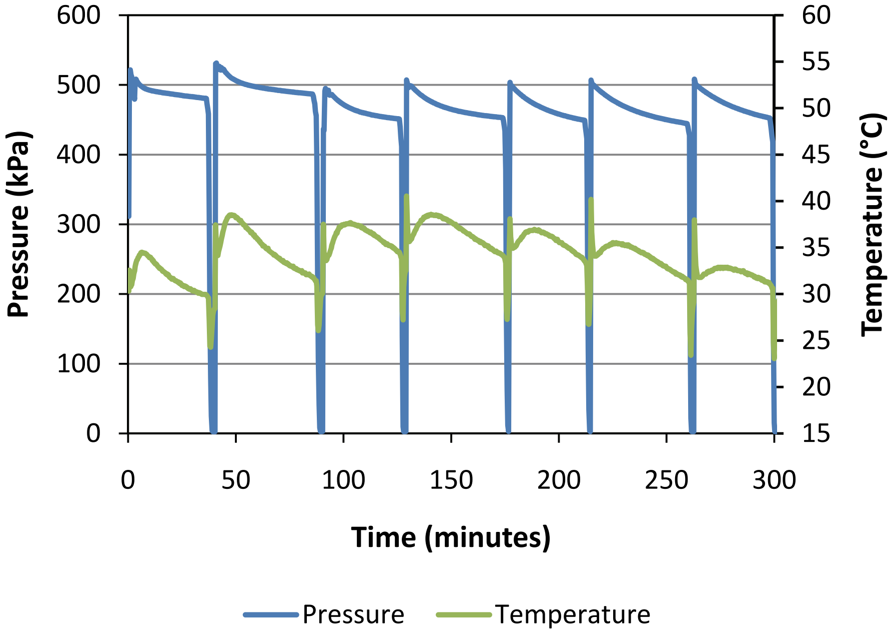

Figure 6.4: Cyclic injection flue gas carbonation of cement paste

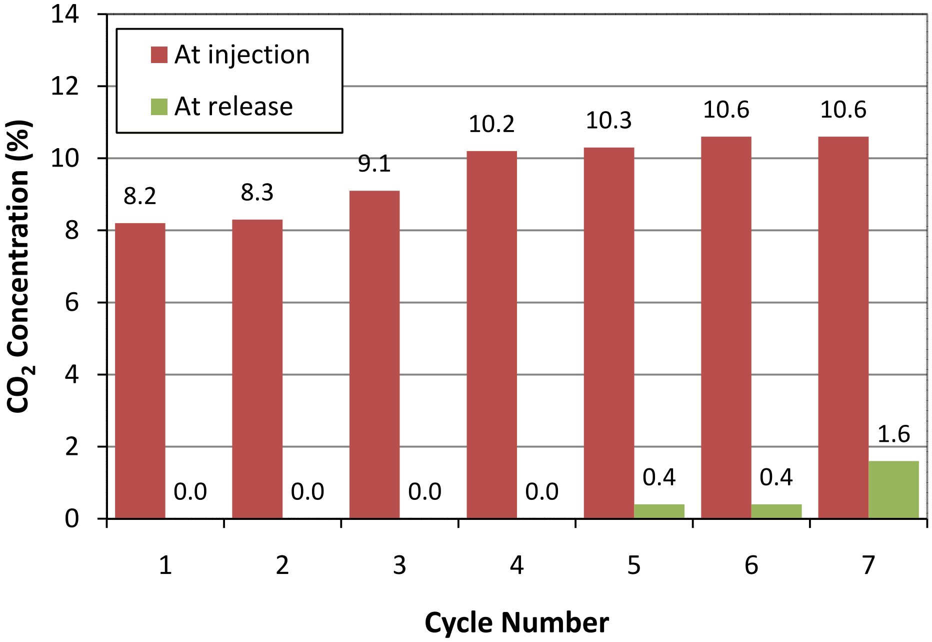

Figure 6.5: Reaction chamber CO_2 concentration in a cyclic injection procedure

Chapter 7

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CONCLUSIONS

CONCLUSIONS

The carbon dioxide uptake and performance of carbonated concrete was studied to investigate the feasibility of carbon dioxide sequestration through carbonation-curing of cementitious products. Paste, mortar and concrete samples were examined to quantify such aspects as the carbon dioxide absorption, strength development, and durability of carbonation-cured concrete.

1) The carbonation-curing of six cementitious materials (Type 10 cement, Type 30 cement, GGBF slag, EAF slag, fly ash and calcium hydroxide) showed that their carbon uptake capacities were a significant fraction of their theoretical maximum. The degree of reaction of the GGBF slag was nearly 20% of what the chemistry indicated was possible. The carbonation degree of the cements was 25%, the EAF slag was near 30%, the fly ash exceeded 45% and the calcium hydroxide exceeded 50%. There was little difference in the carbonation behaviour of binder treated in a compact or in a powdered form indicating that porosity of the compacted samples was not a critical limiting factor for CO_2 uptake.
2) Mass gain was used as a way to quantify carbonation uptake. The mass gain results compared well with the net increase in CO_2 as measured by infrared or thermal analysis. The use of mass gain to quantify carbon uptake is advantageous in that it is a simple and quick method that avoids sampling bias by measuring the entire specimen rather than destructively taking a cored sample.
3) Carbon dioxide could be successfully sequestered into manufactured fine aggregates and provides a novel and easy way of storing CO_2 in concrete products. Ladle slag was treated with carbon dioxide. The carbonated slag was then used as a fine aggregate in

both hydrated and carbonation-cured mortar and compared to similar mortars that employed a conventional fine aggregate. A carbonation-cured river sand mortar contained about as much carbon dioxide as was in the hydrated mortar as part of the carbonated ladle slag sand and proves that the sequestration gains associated with more technically complex carbonation-curing can be achieved by simply using a carbonated slag sand in a conventionally hydrated product. A carbonation-cured slag sand mortar contained almost twice as much (on the basis of the amount of binder) sequestered CO_2 as the hydrated mortar containing the carbonated slag sand. While the slag sand is an easy and energy efficient way of sequestering CO_2 into a concrete product, an additional carbonation-curing step can double the amount sequestered.

4) Products made with carbonated ladle slag aggregates and subsequently hydrated were as strong as products (made of either type of sand) subjected to only hydration, but were slightly weaker than the comparable carbonation-cured river sand sample. Products made with carbonated slag aggregates were shown to have a higher CO_2 absorption capacity in subsequent carbonation-curing than did the products made with conventional aggregates. Either the carbonated aggregate had the ability to absorb further carbon dioxide from the carbonation-curing step, or the porous slag sand allowed a better penetration of CO_2 gas into the sample. The high water absorption of the slag sand would make it suitable for an application such as internal curing which utilises a porous, lightweight saturated aggregate to combat self desiccation of hydrating concrete.

5) Carbonation of the ladle slag reduced the amount of extractable CaO to a level below that of the cement used in the study. Grinding of the carbonated slag and retesting the extractable CaO content revealed that some CaO could still be found inside the particle

but it had not been extracted when subjected to the original, aggressive, test. The carbonation does not consume all of the CaO in the particle but considerably reduces the potential for a deleterious lime hydration expansion later.

6) Concrete cured 2 hours under 100% CO_2 at 150 kPa was shown to performed favourably as compared to hydrated concrete. Four different binders were used: OPC, an 85/15 slag cement, a 75/25 OPC/GGBF slag blend and a 50/50 OPC/GGBF slag blend. The strength of concrete strength after a carbonation treatment of two hours was over 70% of the 24 hour hydration strength. No significant difference was observed in the 28 day moist cured strength of the carbonated and hydrated concretes demonstrating that the carbonation treatment offers the benefit of binding carbon dioxide and increasing very early strength without compromising 28 day strength. The carbonated concretes were slightly stronger after 120 days of moist curing for the OPC and 75/25 blends. The carbonated concrete was weaker in the 50/50 blend. The strengths of the carbonated concretes were higher than the hydrated concretes after 120 days limewater immersion in all cases except for the 50/50 GGBF blend. The high slag substitution, and the higher degree of carbonation of the cement in this concrete, served to reduce the secondary cementitious nature of the slag and the related strength development. The fracture toughness of the carbonated and hydrated concretes were comparable when tested after 120 days of hydration.

7) The average carbonation uptake, as measured by mass gain, of the concretes was around 9%. The 50/50 GGBF slag blend concrete had the highest mass gain, 10.5%, despite having a chemistry that had a lower carbonation capacity than the other concretes. The high slag content was suggested to either permit the vigorous carbonation of cement to take place with fewer competitive sites (see further in Appendix 1) or to allow the CO_2 to

penetrate deeper into the sample before ingress was slowed by the buildup of carbonation products. Despite the increase in carbonation, the lower strength of the 50/50 blends indicated that the development of effectively strong and uniform carbonated microstructures was hindered.

8) The durability of the concrete was improved by carbonation-curing. All of the carbonated concretes passed the freeze/thaw durability test while all of the hydrated concretes failed. The pH of the carbonated concrete was reduced but was still above the level required for the passivation of iron. The 50/50 GGBF blend concrete had the lowest pH at about 11.6. Significant improvement in the weathering shrinkage resistance of concretes with 25% or 50% GGBF slag was observed.

9) The annual North American production of five considered products (concrete masonry units, concrete pavers, cement mesh board, cement fibre board, and ladle slag for use as a fine aggregate) was estimated to have the capacity to annually absorb 2.0 million tonnes of CO_2 when carbonated using recovered CO_2 or 0.98 million tonnes when using flue gas. The estimated single site sequestration in the daily production of these products ranged from 3.3 to 70.3 tonnes of CO_2. An annual sequestration of 2 million tonnes of CO_2 compares favourably to the largest scale geologic sequestration projects that have an annual storage on the order of 1 million tonnes. However, while geological storage at a single site would operate over a set period and to a specific capacity, the sequestration of carbon dioxide into concrete products can operate for decades to come.

10) The use of recovered CO_2 for carbonation-curing was found to offer favourably low emissions and thus a high net sequestration of CO_2. The higher CO_2 emissions factors for electrical energy production in the United States means that the recovery, compression

and use of carbon dioxide on site would have a net efficiency of 82.6% while in Canada it would be 93.7%.

11) The transportation of recovered CO_2 would likely be required to move the recovered carbon dioxide from the point source emitter to the precast concrete location where it would be employed in carbonation-curing. A net sequestration efficiency of 80.7% in the United States and 91.7% in Canada could be achieved if the process included road transportation of the recovered CO_2 150 km.

12) The energy required, on the basis of CO_2, to compress flue gas for carbonation-curing increases greatly with pressure due to the low carbon dioxide concentration. The emissions related to compressing flue gas exceed those of preparing recovered CO_2 if the flue gas is used at a pressure above 300 kPa. The net sequestration efficiency at 400 kPa would be 80.2% in the United States and 92.8% in Canada.

13) The carbonation-curing of a tonne of cement in a concrete building product could feasibly reduce the associated specific emissions (emissions per tonne of binder) by 18% from 670 kg CO_2/t cement to 550 kg CO_2/t cement. If the net emissions of the curing were also considered (see Appendix 2), then the specific emissions of carbonation-cured concrete would be about 30% lower than the emissions for steam cured concrete. If the binder included 25% of the cement replaced by slag then the total specific emissions would be halved. 70% emissions reduction could be achieved with 50% cement replacement by GGBF slag but the effect of carbonation-curing on the long term strength development would have to be considered.

14) The capital cost for the recovery of carbon dioxide would be a significant obstacle to the adoption of carbon curing in the precast industry. The infrastructure cost of implementing

point source recovery of CO_2 is currently estimated to cost about $2.5 million. While cheaper and smaller scale capture technology is likely to be developed, the cost of today’s technology would likely be prohibitive for existing cement plants or precast producers. However, in the short term, the technology is implementable by buying liquid CO_2 as an industrial gas (with costs on the order of $40-80 per tonne). In the longer term, CO_2 recovery at coal-fired power plants would produce large amounts of recovered CO_2 and provide opportunities for it to be widely available and seeking a beneficial use.

SUGGESTIONS FOR FUTURE WORK

The presented work has highlighted several areas that would benefit from further study.

1) The extension of carbonation-curing to reinforced precast concrete should be considered. The pH reductions associated with the immediate carbonation of concrete were shown to not be grounds for concern in terms of reaching a low enough pH that the despassivation of ferrous reinforcement would occur. The potential sink for 2.0 million tonnes of carbon dioxide could be increased by considering new product segments.
2) The level of GGBF replacement influences the pozzoloanic activation of the slag in a carbonation-cured concrete. Cement replacement at 25% does not seem to have any affect on the properties. Replacement at 50% encounters problems with strength development. Whether there is an insufficient amount of cement or the pH is too low the secondary cementitious nature is reduced. If 50% replacement is problematic then perhaps a level between 25% and 50% would provide an optimum of cement replacement and performance. Using slag is an important and easy way to improve the emissions associated with a carbonation-cured concrete product.
3) The concrete produced in this study was appropriate for the research performed. The formulation of commercial precast concrete products is something that producers protect as a matter of trade practice but efforts should be made to study actual precast concrete products rather than simulated versions. Additionally, the curing of the concrete in the study was ideal in that the sufficient moisture was supplied either through moist curing or limewater immersion. Concrete, in actual practice, rarely receives ideal curing. Extended moist curing of precast concrete is not commercially viable. It is necessary to examine

the long term strength development of carbonation-cured concrete that is subjected to subsequent curing in air.

4) Ladle slag has been considered for use as a carbonated fine aggregate but there are other waste materials that could be carbonated and serve a similar role. Even if the carbonated waste materials were not employed as a construction aggregate, the carbonation treatment could still be employed to pre-treat materials meant for landfills. The slag could be treated directly with flue gas (with blast furnace or steel making flue gas with a CO_2 content on the order of 20%) rather than stockpiling and weathering the slag (using the atmospheric CO_2 with a concentration of about 0.04%). The development of a cap and trade carbon economy will bring about a ready economic benefit for the avoidance of emissions and if carbon dioxide can be removed from flue gas by reacting it with a waste material then it would be an easy approach to follow.

5) The possibility of using carbonation to address the free CaO content of ladle slag should be extended to long term durability testing of the slag aggregate. Conventional accelerated volume stability testing subjects samples to high temperature and humidity. A successful test of carbonated slag with such a procedure would expand the evidence that carbonated slag can be used as a fine aggregate.

6) The promise of sequestered carbon dioxide in manufactured aggregates is the simplest approach to sequestering carbon dioxide into concrete. Carbonated aggregates could be used in all types of concretes. Using carbonated slag aggregate in cast-in-place concrete merits attention. The effect of the aggregates on the fresh concrete properties would have to be studied as well as its effect on concrete durability.

7) The presented research showed that the smallest particle sizes are the most efficient at absorbing carbon dioxide. The 5% limit on microfines (particles < 75 μm) in concrete aggregates has been suggested to be unnecessarily low and increasing the fraction of fine particles would increase the amount of carbon dioxide that can be put into concrete as a part of the aggregates. This should be studied.

8) The promise of using flue gas should be investigated further. The approach is simpler in that it can involve only gas compression and avoid the effort of recovering and transporting carbon dioxide. If the infrastructure investment is a barrier to the use of recovered CO_2 in a carbonation-curing scheme then reduced complexity of flue gas carbonation offers some hope that carbonation-curing can be readily pursued. Improving the carbonation uptake achievable with the use flue gas would greatly benefit the concept of carbonation-curing.

STATEMENT OF ORIGINALITY

While previous work has used early-age carbonation to achieve rapid early strength development of concrete, the presented work systematically studied the carbon uptake capacities of binders, and their mortar and concrete in an attempt to maximize the carbonation uptake while enhancing performance in concrete products. Optimizing the net sequestration considered the gas pressure (atmospheric vs. 1.5 bar vs. 500 kPa), gas concentration (recovered CO_2 vs. flue gas), and mix design (substitution of cement by GGBF slag, compaction load, water to binder ratio).

A novel use for a calcium-rich waste, ladle slag, was developed by employing it as a fine aggregate in concrete. The carbonation treatment eliminated calcium hydroxide and free CaO in the slag, solidified carbon dioxide as solid $CaCO_3$ and converted the slag from an industry waste to a useful, value-added, form. The performance of the slag sand was compared favourably to a regular fine aggregate. The ladle slag sand would be a reasonable alternative to conventional sands while serving to sequester significant amounts of carbon dioxide.

The carbonation-curing of concretes with blended cement/GGBF binders was examined. The effect of early age carbonation on both the short and long term activation of slag in concrete was examined. The use of slag is an accepted way to reduce the specific CO_2 emissions associated with a cementitious building product. The research showed that strength development of carbonation-cured slag blends was comparable to, or better than, that of hydrated blends if the cement replacement by slag was 25% or less. The durability (freeze/thaw resistance and weathering shrinkage) was improved by carbonation-curing for all slag contents.

A comprehensive energy analysis (including recovery, compression, liquefaction and transport of carbon dioxide) for a potential carbonation-curing scheme was performed and demonstrated the viability of carbonation-curing as a carbon dioxide sequestration methodology.

The potential capacity for CO_2 sequestration in the carbonation-curing of the North American production of various types of precast concrete products was estimated. The proposed future integration of carbonation-curing into cement and concrete production is feasible. The total energy consumption, and related CO_2 emissions, is much less for carbonation-curing than for steam curing or autoclaving

Appendix 1

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THE USE OF LADLE SLAG AS A CEMENT REPLACEMENT IN CARBONATION-CURED AND HYDRATED CONCRETE

The work with blended cements presented in Chapter 5 omitted research that was performed with ladle slag. The amount of ladle slag available only permitted a partial research program to be completed.

Concrete was produced with 25% cement replacement by as-received ladle slag with a particle size <75 μm. As with the work presented in Chapter 5, the fine aggregate was river sand, the coarse aggregate was crushed granite, the aggregate to binder ratio was 4:1, and the coarse to fine aggregate ratio was 1:1, the water to binder ratio was 0.26 was selected. The sample compaction load was 12 MPa. Carbonation cured samples were treated with CO_2 at a pressure of 150 kPa for 2 hours immediately after moulding. Samples were hydrated by storing them in a moisture chamber with a relative humidity of 87%.

Compressive strength was tested immediately after the two-hour carbonation as well as after a subsequent hydration of 24 hours and 28 days. Reference samples were tested after hydration in a moist environment up to 24 hours and 28 days. Freeze/thaw durability and weathering shrinkage tests were also performed.

The average carbonation mass gain of the ladle slag blend concrete was 8.1%. This was the lower than the OPC concrete (9.3%) and lower than the slag cement (8.7%) which had shown the lowest carbonation mass gain of the four types of concrete discussed in Chapter 5. The ladle slag had a CO_2 uptake comparable to the cement (as shown in Chapter 4, the ladle slag < 75 μm carbonated for 2 hours at 500 kPa achieved a mass gain that exceeded 15%). In contrast to the addition of the less reactive GGBF slag serving to increase the uptake of the concrete (75/25 blend reached 9.6% mass gain and 50/50 blend reached 10.5%), the slag in this case would have been reacting with CO_2 competitively with the cement and would have likely lead to the quicker formation of enough carbonate reaction products to slow the penetration of gas into the concrete and the associated carbonation reaction. The grading of the ladle slag may have also provided some larger particles that improved the packing of the binder fraction and further accentuated the competitive carbonation reactions of adjacent particles.

The strength of the carbonation cured ladle slag concrete at two hours was only 4.5 MPa or slightly more than 50% of the 2 hour strength of the carbonation cured OPC concrete (Figure A1.1). Subsequent hydration to 24 hours results in an increase in strength of 118% to give a strength comparable with the ladle slag concrete hydrated to 24 hours. This was comparable to the strength of the carbonated OPC concrete at 24 hours but the hydrated OPC control was about 15% stronger. The carbonated ladle slag blend was 19% stronger than the sample comparable hydrated sample at 28 days. It was also significantly stronger than both of the OPC concretes.

The pH of the hydrated ladle slag concrete was about 12.6 while the pH of the carbonated one was 12.4. The pH reduction of the ladle slag concrete was only about 0.2 or about half of the carbonated OPC, slag cement and 75/25 GGBF blend concretes discussed in Chapter 5. The absorption of the hydrated ladle slag concrete, 8.8%, was reduced to 8.3% after carbonation treatment. This was consistent with the small reductions in absorption seen in the other concretes.

The freeze/thaw performance of the ladle slag concrete was improved by carbonation curing but it did not meet the specification. The hydrated concrete samples had enormous mass losses within 10 freeze/thaw cycles and completely disintegrated before the 25 cycle test was completed. The carbonation cured sample remained intact until the completion of the test but showed and average loss of 1076g/m^2, which was more than 5 times the acceptable limit of 200 g/m^2. The weathering shrinkage of the ladle slag was significantly improved. It was reduced from about -310 με in the hydrated sample to -115 με in the carbonation cured specimen.

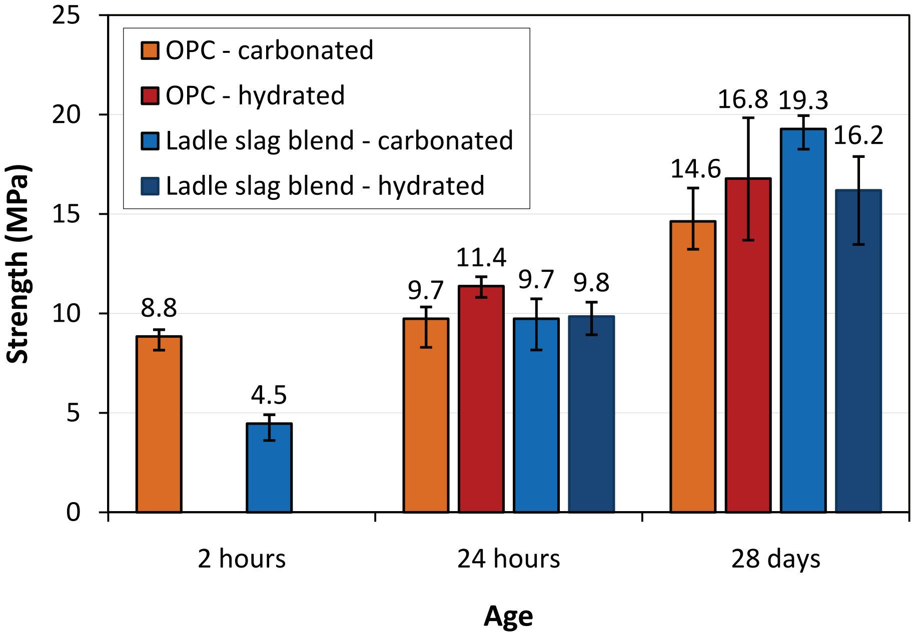

Figure A1.1: Compared compressive strength of OPC concrete to ladle slag blend concrete carbonated for 2 hours prior to hydration and subject only to hydration

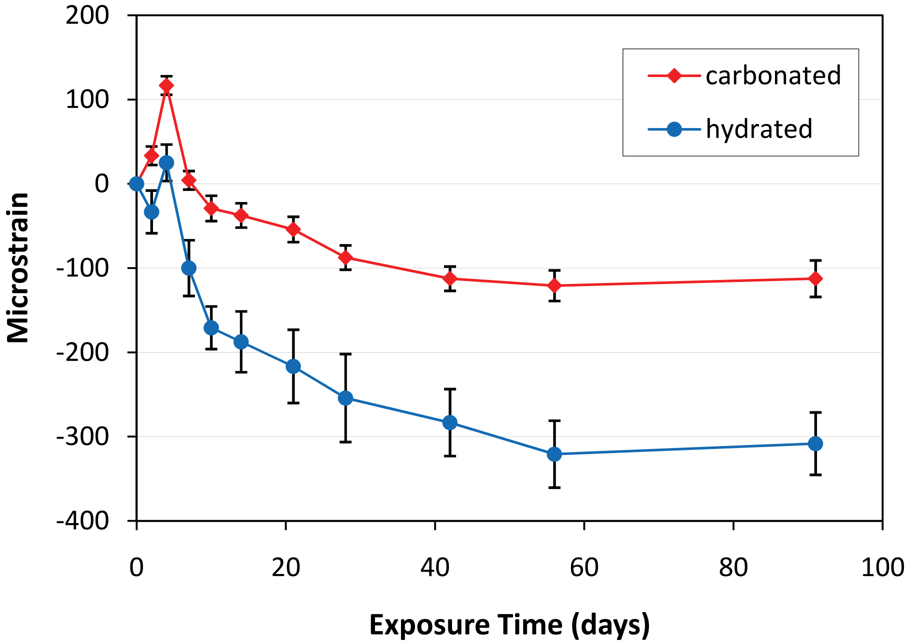

Figure A1.2: Weathering shrinkage of carbonation cured and hydrated 75/25 ladle slag blend concrete

Appendix 2

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A COMPARISON OF THE NET EMISSIONS ASSOCIATED WITH CARBONATION-CURING AND STEAM-CURING

Combining the work in Chapter 5 and Chapter 6 allows a comparison to be made between the net emissions related to carbonation cured and steam cured concrete. The following assumptions have been made:

- Specific emissions for the binder are assumed to be 670 kg CO_2/tonne of cement and encompass both the emissions related to calcination of the raw materials and the thermal energy required for the process. Slag is considered as a waste material with no associated CO_2 emissions. The slag cement is considered to be 15% slag. (Figure A2.1)
- The carbon uptake, expressed as a percentage of the original binder, for the various types of concrete are as reported in Chapter 5. OPC = 9.3%, Slag cement = 8.7%, 75/25 blend = 9.6% and 50/50 blend = 10.5%
- Carbonation curing emissions are at the USA off site curing rate for recovered CO_2: 193.8 kg CO_2 emitted per tonne of CO_2 processed. One tonne of CO_2 sequestered is considered to be one tonne processed. The net curing emissions are the difference between the amount of CO_2 absorbed by the concrete and the amount of CO_2 emitted while processing that amount of sequestered CO_2. (Figure A2.2)
- Steam curing emissions are 38.5 kg CO_2/m^3 concrete. On the basis of concrete with a density of 2200 kg/m^3 and containing 220 kg of cement, the emissions would be 175 kg CO_2/tonne of cement.

The specific emissions (emissions on the basis of a tonne of cement) of a carbonation cured concrete are significantly lower than those of a steam cured concrete (Figure A2.3). A tonne of cement in steam cured OPC concrete will have and overall specific emission of 845 kg of CO_2. The carbonation curing of OPC concrete will have specific emissions that are 29% lower at 625 kg of CO_2. The use of blended cement reduces the emissions even further. The slag cement emissions are 40% lower, the 75/25 GGBF blend emissions are 49% lower and the 50/50 GGBF blend emissions are 70% lower.

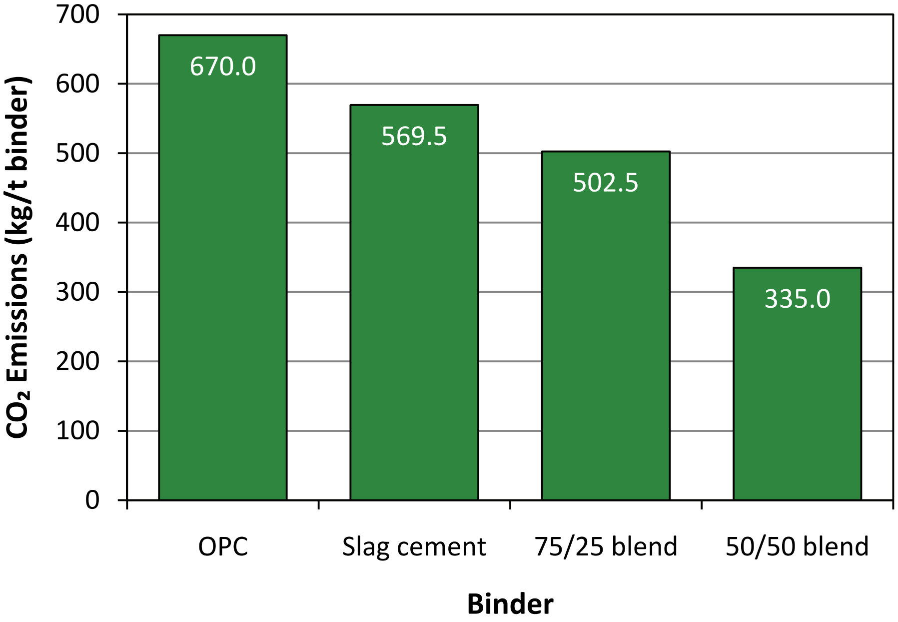

Figure A2.1: Specific CO_2 emissions related to four types of concrete binders

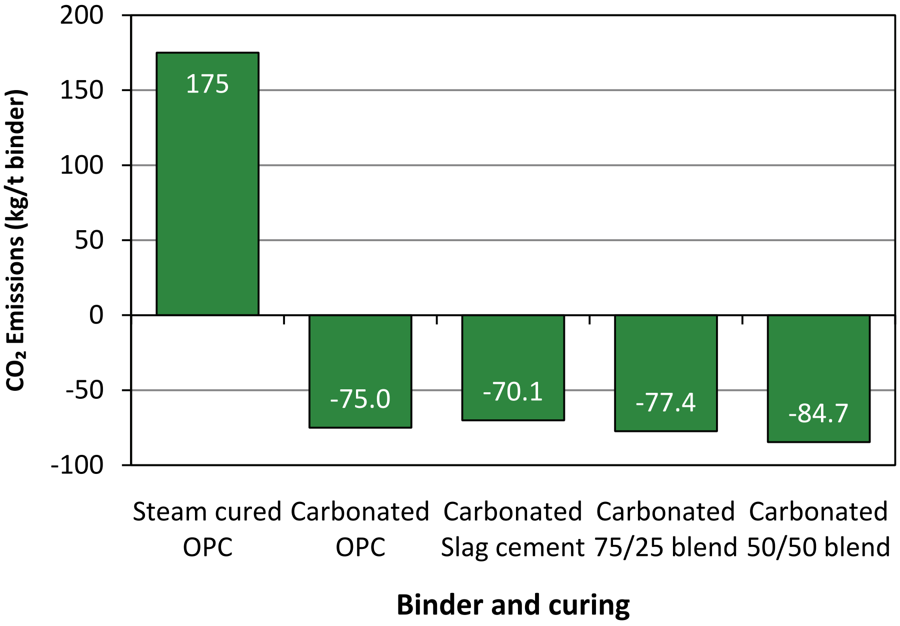

Figure A2.2: Specific CO_2 emissions related to the curing of five types of concrete

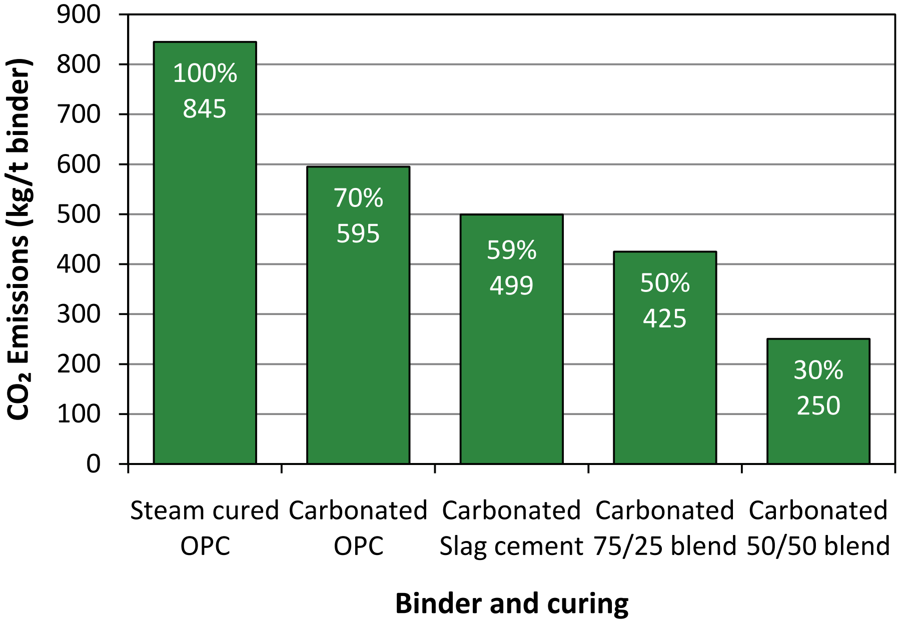

Figure A2.3: Overall specific CO_2 emissions related to five types of concrete