Coventry University and The University of Wisconsin Milwaukee Centre for By-products Utilization, Second International Conference on Sustainable Construction Materials and Technologies June 28 - June 30, 2010, Università Politecnica delle Marche, Ancona, Italy. Main Proceedings ed. J Zachar, P Claisse, T R Naik, E Ganjian. ISBN 978-1-4507-1490-7 http://www.claisse.info/Proceedings.htm

Market Analysis of CO₂ Sequestration in Concrete Building Products

Yixin Shao, Sean Monkman and Sam Wang

Department of Civil Engineering, McGill University, Montreal, Quebec Canada H3A 2K6, Email: < yixin.shao@mcgill.ca>, <sean.monkman@mail.mcgill.ca>, <sam35wang@yahoo.ca>.

ABSTRACT

Four typical cement based building products are studied for their abilities to sequester carbon dioxide through early age carbonation curing. They are concrete blocks, paving stones, expanded polystyrene bead (EPB) cement boards and cellulose fiber boards. Carbonation curing takes place in a chamber under a pressure of 500 kPa, at ambient temperature, for duration of 2 hours. Pure carbon dioxide gas is used to simulate the recovered CO_2 from point sources. Carbon uptake, immediate strength gain and long term strength development are measured. It is found that the uptake is dependent on the type of products, water cement ratio and porosity. In the United States and Canada, the annual cement consumed in their productions is about 14 million tonnes. If all of these products were carbonation cured then the net annual sequestration of CO_2 would reach 1.8 million tonnes of CO_2 . The proposed process offers a feasible method of safe and permanent sequestration of carbon dioxide in manufactured concrete products.

INTRODUCTION

Carbon sequestration has been identified as an important greenhouse gas mitigation strategy for addressing anthropogenic carbon dioxide emissions. One challenge currently facing carbon sequestration is to find beneficial uses of recovered CO_2 .

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 several calcium-carrying materials had the capacity to bind CO_2 into CaCO₃ [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 captured carbon dioxide.

Carbonation curing of concrete also offers technical benefits for the final products. The rapid strength gain by carbonation prompted research on its mechanism [Berger et al. 1972; Young et al. 1974]. The carbonation curing 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]. However there has not been any large-scale industry implementation of the process, probably due to the cost of producing carbon dioxide gas. It is possible that this obstacle would be removed in the near future when, prompted by the development of large-scale CCS, carbon dioxide of high purity becomes a by-product from hydrocarbon-based power generation or cement production.

The purpose of this paper is to identify commercially available precast concrete building products (that do not contain ferrous reinforcement) that are suited for carbonation treatment. An estimate of the amount of carbon that can be consumed by such products and suggestions on how these processes could be integrated into existing production are discussed. The concrete curing process is developed to be able to employ recovered CO_2 with high concentration. The process is evaluated based on carbon uptake and performance gain.

EXPERIMENTS

Candidate 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 varied capacities to bind carbon dioxide. It is particularly 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 fibreboards. These products are mass produced, require special curing treatments, and can realize several benefits through carbonation curing.

Sample Preparation

Concrete masonry blocks and paving stones were formulated with a similar proportion except that the former had a cement content of 10% and the latter 20%. Water to cement ratio of 0.25 was used to achieve a dry mix for compact forming. The constituents were mixed for approximately 5 minutes and samples were formed under a pressure of 10 MPa to make compacts of 76 mm by 127 mm by 25 mm thick.

Cement bead board comprised cement paste and expanded polyethylene beads at a volume ratio of 40 to 60. Cement and EP beads, 90% of which had a diameter of about 2.36 mm, were mixed with water at a water to cement ratio of 0.36 and a superplasticizer to cement ratio of 0.5%. The samples were formed by conventional casting to simulate the commercial production of 12 mm thick bead board. The cast bead boards were subject to a drying process of 30 minutes at 60 °C before carbonation.

Cellulose fiber boards were produced using slurry-dewatering process. After being soaked overnight with 1.2 Litre water for each batch, fibers were mixed with cement, forming a slurry by adding cement gradually during mixing. After mixing for 20 minutes, the excessive mixing water in slurry was filtered out so that a workable fiber-cement mixture was formed. Fiber boards were compact formed at 0.7 MPa followed by a drying of 150 minutes at 60 °C.

Portland cement paste was also tested. It was mixed with water at a water cement ratio of 0.15 for 5 minutes, and compressed at a 0.7 MPa to form compacts of 76 mm by 127 mm with a thickness of 12 mm. Cement paste batches served as a matrix reference for the fiberboards with the same compact pressure.

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.

Pressurized carbonation curing system

The pressurized carbonation curing setup is shown in Fig. 1. The open-inlet system consists of high purity CO_2 introduced into a sealed chamber with the inlet gas valve left open to ensure a continuous supply of carbon dioxide. Precast products are placed into the chamber immediately after their formation with the curing gas injected up to a pressure of 500 kPa. 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 about two hours beyond which the reaction slows down and uptake efficiency is not improved (Shao et al. 2006). Although the gas pressure in the chamber in maintained constant for the processing of different concrete products, the peak temperature varies depending on the cement content of the product.



Fig. 1: Carbonation curing setup using pressurized recovered CO₂

Quantification of CO₂ Uptake

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

$$CO_2 \text{ Uptake (\%)} = \frac{(Mass_{afterCO2} + Water_{lost}) - Mass_{beforeCO2}}{Mass_{drybinder}} = \frac{\Delta Mass}{Mass_{drybinder}}$$
(1)

Second method to quantify CO_2 uptake is the mass curve method. Mass curves are obtained using an electronic balance (Fig. 1) to record in-situ mass gain of the precast samples as a function of time during the entire carbonation process. The balance is zeroed after the samples are placed and vessel is sealed. The mass gain is recorded from the moment the gas was injected. For the open system of pure CO_2 carbonation, the tank valve is kept open after gas injection, and a constant gas pressure is maintained by the regulator. Therefore the mass gain of the system during carbonation is an indicator of CO_2 uptake. After the gas is released to the atmospheric pressure in the end of process, the residual mass recorded by the balance represents the overall CO_2 mass uptake.



Fig. 2: Temperature and pressure curves of precast products

Temperature curves and mass curves

The typical pressure and temperature curves of carbonated four precast products are shown in Fig. 2. Temperature curves reflected the carbonation intensity and can be used to examine the carbonation kinetics during the carbonation process. Although the carbonation pressure was maintained nearly a constant, the peak temperatures were quite different from each other.

Fig. 3 shows the corresponding mass curves as CO_2 uptake by the products. Although high peak temperature usually indicates a high carbonation reaction, it is not necessarily related to a higher CO_2 mass uptake. Cement paste has the highest heat release. Its carbon uptake however is lower than fiberboard. Cement bead board reacts with carbon dioxide in a similar manner as concrete does. Mass curves also clearly demonstrate that majority of reaction in cement paste, cement bead board and concrete occurs in first 30 minutes while reaction in fiberboard lasts longer than one hour, resulting in a significantly higher uptake in fiberboard. The end values of mass curve represent the CO_2 uptake in the given period.

RESULTS

CO₂ sequestration in 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. CO_2 uptake by masonry units was estimated 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 $76 \times 127 \times 25$ mm. The fresh samples were placed in the curing chamber immediately after being formed and were subjected to recovered CO_2 for two hours with constant pressure of 500 kPa. The absorption of carbon dioxide, by mass of cement binder, was about 9.8%. The strength after two hours carbonation reached 78% of 24-hour hydration strength and was 440% of the twohour hydration strength.



Fig. 3: Mass curves of precast products subject to carbonation curing

The North American market for CMUs is predicted to increase to 4.3 billion units in 2010 (Freedonia Group 2006). 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). 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 on the order of 52.9 tonnes. Carbonation curing using recovered CO_2 would consume 5.2 tonnes of CO_2 per day.

CO₂ sequestration in 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/m³ 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 eliminates 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/m³, and a cement content of about 20%, then about 2.6 million tonnes of cement is 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 CO₂ would bind about 254,800 tonnes of carbon dioxide.

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 .

CO₂ sequestration in fibreglass mesh reinforced cement bead board

Fibreglass cement backboard consists of an aggregated cement based core matrix, reinforced with glass fibre 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/m³ 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, a carbonation treatment can reduce the pH value of the cement matrix, protect glass meshes from alkali attack and lead to more durable products.

The CO₂ uptake by mesh reinforced cement board was investigated in the lab. The mixture had a water to cement ratio of 0.35 and a cement content of 70%. 12-mm thick mesh-cement samples 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 two hours, yielding a CO₂ absorption of 12.2% based on cement mass.

It is estimated that the production capacity of mesh cement board in US and Canada is approximately 75 million m²/year (Venta 2000). If formulations can be assumed to have a thickness of 12.7 mm, a density of 1250 kg/m³, 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 CO₂ uptake will be 72,590 tonnes per year with recovered gas. A single plant producing 9,570 m²/day would use 76 tonnes of

cement. The estimated carbon dioxide uptake when curing with recovered CO_2 would be 9.3 tonnes.

CO₂ sequestration in cellulose fibre board

Cellulose fibre 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/m³. The production follows the traditional Hatschek (slurry-dewatering) process. Typical fibre cement consists of 52% cement, 32% sand, and 8% pulp. The board is formed by slip casting, dewatering, laminating and compact forming. The fibre 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 fibreboard requires both pre-curing and autoclave curing, this process could be possibly replaced by carbonation curing to provide both accelerated hydration and carbon sequestration. The carbonation can also provide some technical advantages such as reducing the pH of the cement matrix which would serve to protect the cellulose fibres from alkali attack and thus inhibit the aging process.

For the recovered gas and a fibreboard with 12% fibres, two hours of carbonation using the open-inlet system achieved a CO_2 uptake of 18.9%. The 2-hour modulus of rupture (MOR) by carbonation 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.

The annual North American fibre cement production is about 910 million $m^2/year$ (9.8 billion sf/yr (James Hardie Industries 2008)). Assuming a typical thickness of about 8 mm (5/16^{cc}), a density of 1500 kg/m³ and a cement content of 48%, the annual production represents the consumption of approximately 4.8 million tonnes of cement. If the total fibre cement production was carbonation cured, the annual carbon dioxide storage in fibre cement could reach 907,200 tonnes using recovered CO₂. 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 m² with a cement requirement on the order of 400 tonnes. If the production is carbonation cured, then the daily uptake at one plant would be 75.6 tonnes using recovered CO₂.

CO₂ Sequestration Potential

The results are summarized in Table 1. The total capacity of carbon sequestration in four typical concrete products produced in United States and Canada can reach about 1.8 million tonnes per year. This is approximately equal to two new projects of carbon capture and storage (CCS) in geologic formation.

The proposed carbonation curing process offers a feasible method of safe and permanent sequestration of carbon dioxide in manufactured concrete products. 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).

	CMU	Paver	Mesh board	Fibreboard
Annual production	4.3×10^9 units	$74 \times 10^6 \mathrm{m}^2$	$75 \times 10^6 \text{ m}^2$	$9.1 \times 10^8 \text{ m}^2$
Cement used in product (Mt)	5.9	2.6	0.595	4.8
CO ₂ Uptake, %	9.8%	9.8%	12.2%	19%
Sequestration potential from recovered CO ₂ (Mt)	0.578	0.255	0.073	0.907
Two-hour carbonation strength (MPa)	10.3±0.6	10.3±0.6	7.8±0.2	10.5±1.2
28-day strength (MPa)	20.5±0.9	20.5±0.9	7.8±0.5	11.7±0.5

 Table 1: Annual CO2 sequestration potential by concrete products made in United States and Canada

CONCLUSIONS

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 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.

REFERENCES

- Berger, R. L., Young, J. F., and Leung, K. 1972. Acceleration of hydration of calcium silicates by carbon-dioxide treatment. Nature: Physical Science, 240: 16-18.
- Freedonia Group. 2006. Annual masonry unit demand edging toward 15 billion units. Concrete Products, 109(9), PC3.
- ICPI. 2007. North American paver sales tops 800 million square feet in 2006 [online], <u>http://www.icpi.org/myproject/ConcretePaverSalesTops800MillionSquareFeet.pdf</u>.
- IPCC. 2005. IPCC special report on carbon dioxide capture and storage. Prepared by working group iii of the intergovernmental panel on climate change, B. Metz, O. Davidson, H. de Coninck, M. Loos, and L. Meyer, eds., Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 431 pp.

- James Hardie Industries N.V. 2008. Annual report 2008. James Hardie Industries, Australia. Available from <u>http://www.ir.jameshardie.com.au/jh/artable.jsp</u>.
- Johnson, D. 2000. Accelerated carbonation of waste calcium silicate materials. SCI Lecture Papers Series, <u>http://www.soci.org/SCI/publications/2001/pdf/pb76.pdf</u>.
- Monkman, S., and Shao, Y. 2006. Assessing the carbonation behavior of cementitious materials. Journal of Materials in Civil Engineering, 18(6): 768-776.
- Monkman, S., Shao, Y., and Shi, C. 2009. Carbonated ladle slag fines for carbon uptake and sand substitute. Journal of Materials in Civil Engineering, 21(11).
- Shao, Y., Mirza, M. S., and Wu, X. 2006. CO₂ sequestration using calcium-silicate concrete. Canadian Journal of Civil Engineering, 33(6): 776-784.
- Toennies, H. T. 1960. Artificial carbonation of concrete masonry units. Journal of the American Concrete Institute, 31(8): 737-755.
- Venta, G. J. 2000. Glass fibre mesh reinforced cementitious boards: The other cement boards. *In* Proceedings of the 7th Int. Conf. on Inorganic Bonded Wood and Fibre Composite Materials, Sun Valley, Idaho, 3-14.
- Young, J. F., Berger, R. L., and Breese, J. 1974. Accelerated curing of compacted calcium silicate mortars on exposure to CO₂. Journal of the American Ceramic Society, 57(9): 394-397.