ABSTRACT

Research was conducted in order to confirm whether carbonation of concrete was a measurable phenomenon in a New Zealand context. With approximately half of the carbon dioxide emissions in the manufacture of cement arising from calcination of limestone [1], the ability of concrete to reabsorb some, or all, of this carbon dioxide has important implications for the cement and concrete industry.

The study found carbonation of New Zealand concrete to be occurring at a similar rate as previous European research. Carbonate titration and phenolphthalein indicator tests were used to test 20 samples consisting of crushed and demolition concrete from Auckland and Christchurch localities dated between 0 and 84 years. The tests determined the extent of carbonation and the relationship that exists between carbon dioxide absorbed and age of the concrete. The results indicate that carbonation increases over time, with the rate the carbon dioxide uptake rapid at earlier ages and progressively slowing with time.

While the study concludes that most of the carbon dioxide emissions from the calcination of limestone during cement manufacturing can be reabsorbed (particularly when aged concrete is crushed for recycling), further research has been planned to determine optimal conditions for carbon dioxide sequestration, and the timeframes over which this can be expected to occur for New Zealand concrete.

Key words: cement, concrete, calcination, life cycle assessment, carbonation

INTRODUCTION

Concrete is often described as an energy intensive building material with a high embodied carbon dioxide (CO₂). However, this view of CO₂ generation from manufacturing in isolation, does not consider the other benefits concrete materials provide using a life cycle assessment approach (LCA) including durability and longevity, thermal comfort, fire resistance, security, ability to recycle, acoustic properties and, of significance to this paper, the potential for uptake of CO₂ [2][3].

A closer examination of the source of embodied CO₂ in the manufacture of concrete indicates that a significant proportion of it can be attributed to the cement manufacturing process. The release of CO₂ from manufacturing cement typically represents 50% from the combustion of fuels and 50% from the calcination of limestone within the kiln process [1].

Generation of CO₂ within the kiln is defined by the following reactions:

\[ \text{Carbon (fuel)} + O_2 = \text{CO}_2 + \Delta H \]
\[ \text{CaCO}_3 + \Delta H = \text{CaO} + \text{CO}_2 \]

Of significance to the sustainability discussion is the ability of cement-based materials (typically concrete) to re-absorb / uptake CO₂ throughout their life. Exposed to air, these materials will absorb CO₂ over time in a process termed carbonation. Carbonation is likely to occur during the service life of concrete, but more importantly will occur rapidly with demolition and reprocessing.

Main carbonation reaction in concrete is given by:

\[ \text{Ca(OH)}_2 + \text{CO}_2 = \text{CaCO}_3 + \text{H}_2\text{O} \]

(Al and Si oxides also contribute to the carbonation of concrete to a lesser extent).

In the past, little thought was given to concrete carbonation, it was recognized as a deterioration mechanism for reinforced concrete structures but design rules were prescriptive, relating purely to concrete strength and cover thickness. However, with modern concrete design, engineers are now able to design the concrete mix and the depth of cover to give the required durability to achieve any specified life of the structure. Typically, for concrete, the design life specified in the Building Code is 50 years for buildings and 100 years for bridges.

The ability of concrete to absorb some of the CO₂ released in cement manufacture as an environmental offset, has only recently been
considered [4]. Theoretically all the carbon dioxide released by calcination of limestone in carbonation of in-service concrete vary with humidity, porosity, water/cement ratio, pozzolanic materials, environment conditions, strength and temperature [5].

More significantly, demolition and crushing of post-service concrete appears to have a very important effect on carbonation during the life cycle of concrete [6]. Demolition and crushing increases the surface areas exposed to the atmosphere and significantly increases the rate of carbonation reactions.

In New Zealand, the continued focus on green building materials, environmental labeling and plans for an emissions trading scheme have highlighted to the cement and concrete industry the need to understand its impacts on climate change from LCA perspective (including post-life). If robust evidence regarding carbonation in New Zealand can be obtained, the cement and concrete industry has a strong case to support the reduction of its traditional carbon footprint.

This paper attempts to document the carbonation of concrete specifically in a New Zealand context. The unique characteristics of New Zealand cement and concrete and climatic / environmental conditions, that materials are exposed to, have the potential cause different rates of carbonation than those previously measured in Europe. The study is empirical in nature, where real-world samples of demolition and crushed concrete are analysed for carbonation.

**METHODOLOGY**

The NZ Portland Cement Association sustainability committee engaged a senior student from the University of Canterbury to undertake this research. The research involved collecting and analysing concrete of various ages to determine the depth of carbonation.

Twenty samples of demolition and crushed concrete were collected from the Christchurch and Auckland areas late in 2007 and early in 2008. The sampling endeavored to be representative of the demolition material and stockpiles. The samples from stockpiles were gathered by the Hand Method (NZS 4407:1986).

Samples taken from some crushed concrete stockpiles were initially problematic as the source and duration of stockpiling was not always obvious. Another challenge in the project was with obtaining demolition and the cement has the potential to be reabsorbed by the concrete during its life [5]. The rates of crushed concrete with an ages less than 15 years. Therefore several examples of newly produced concrete were collected for comparison from core and masonry block.

Once collected, all samples were sealed in plastic bags until they were relocated to the laboratory for testing.

X-Ray Fluorescence Spectroscopy was initially considered as a test method, but later rejected after giving inconsistent results. As an alternative a traditional carbonate titration method [7] was adopted as the main test method for the study.

The titration method involved crushing samples in a primary crusher, before pulverizing into a fine powder. The powder was digested in hydrochloric acid and heated for 3 minutes. Following heating, the solution was titrated with sodium hydroxide and phenolphthalein indicator. The end point was observed when the colour changes from colourless to a light pink. The amount of carbonate present was determined by measuring the volume of sodium hydroxide used for this reaction to occur. It was noted that this titration method gave the result of total carbonates present not just calcium carbonate.

Residual whole concrete samples were also sprayed with a phenolphthalein solution (1g phenolphthalein powder dissolved in 100ml methanol) as a secondary indicator of carbonation. This phenolphthalein test was used to verify the carbonate titration test results and as a method of visually demonstrating the extent of carbonation. After 30 minutes, each sample was photographed as a record and the extent of coloration compared with the titration results. Where a purple colour was observed, little carbonation was assumed to have occurred. Where no purple coloration was observed, a large amount of carbonation was assumed.

The phenolphthalein test method is the basis of the vast majority of carbonation rate data cited in literature [8]. While this method for the determination of the carbonation front has its limitations (it only indicates the pH change in the concrete rather than carbonation), the indicator test was used albeit with an assumed underestimate of the carbonation.
RESULTS

The titration results of the 20 samples are shown in Table 1. Of the samples collected, 16 were from a homogenous source and were age verified. With the exception of the sample from the steps of the Christchurch Woman’s Hospital (later found to be mortar), the titration results showed a clear trend of increasing carbonate concentration with age (Figure 1).

Figure 1 indicates that carbonation occurs quickly initially and then slows over time. Taking a line of best fit for the valid results, a relationship between carbonation and concrete age was established to be $C = 3.9 T^{0.33}$ (where $C$ is percentage of carbonation measured and $T$ is time).

Examples of the phenolphthalein indicator test results displaying a range of concrete ages and physical states are represented in photos 1 - 5.

DISCUSSION

In general the results from the phenolphthalein indicator tests show a good degree of correlation with the titration tests. As a result, a relationship between the age of the sample and amount of carbonate was identified for New Zealand concrete. While additional titration results would have been beneficial to establish a more reliable correlation, the nature and shape of the curve (Figure 1) is consistent with that from previous literature [1].

The results indicate that as time progresses the rate of the carbonation reaction decreases as the carbon dioxide has to diffuse further into the concrete to react. Carbonation is most rapid initially at the concrete surface as it is directly exposed to the atmosphere. Demolition and crushing of concrete significantly helps to increase the rate of carbonation as the surface area is increased and carbon dioxide does not have to diffuse as far.

Given the variation of crushed and demolished concrete collected in the study, the relationship shown in Figure 1 is likely to be representative of carbonation occurring throughout the entire life (ie. both in-service and post-service) of the material.

Results of particular interest included core samples labeled Bombay, RM and Allied which all show a low level of carbonation. In comparison, results from both titration and phenolphthalein tests from the Wallace Block (84 years) and Canterbury Saleyards (60 years) show very high levels of carbonation reflecting their age and state of demolition and crushing. While the cement content of these historic samples remains unknown, it is likely that level of carbonation in the Wallace Block and Canterbury Saleyards material probably represent almost complete carbonation of the original cement content.

One result that was somewhat unexpected was the crushed concrete from the Fulton Hogan Quarry samples. While most of this material appears well-carbonated, other material appears to have experienced little carbonation and retains a purple colour. Given the longevity of these stockpiles, it had been expected that all of this material would have had a reasonable degree of carbonation. However, the uneven carbonation of the stockpiles may be related to carbonation exposure conditions from the face through to the centre of the stockpile or as a result of the inherent differences of source materials.

The 40mm crushed sample from MPL had a higher carbonate value of 12.14%, than the 20mm sample value of 8.77%. The same was true, to a lesser extent, for the Fulton Hogan samples where the 65mm sample had a higher carbonate concentration than the 40mm sample. It would appear that the smaller the crushed concrete, the faster it will carbonate due to the increased surface area. Interestingly, the Norwegian Building Research Institute BYGGFORSK have examined this in some detail (www.danishtechology.dk/building/14460.2).

As part of their research, the recarbonation of varying grades of concrete were examined under laboratory conditions. It was found that 60 – 80% of the CO$_2$ released during calcination has the potential to be chemically reabsorbed by concrete mixtures with w/c of 0.6 or higher for the grain size of 1 – 8 mm within 20 – 35 days of exposure. They also found that coarser aggregate samples carbonated at a significantly slower rate.

Carbonation of the Stevensons masonry blocks appeared to be occurring rapidly. Carbonation at this rate probably reflects the porous nature of the blocks. Modern structural concrete would not be expected to carbonate at a similar rate.

The study observed no obvious difference between samples from Auckland and Christchurch or the different environments in which samples were originally located.
### Table 1: Titration Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age (yrs)</th>
<th>Carbonation %</th>
<th>State</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chch Women’s Hospital (step)</td>
<td>57</td>
<td>24.79</td>
<td>demolition (mortar)</td>
</tr>
<tr>
<td>Wallace Block</td>
<td>84</td>
<td>20.75</td>
<td>crushed</td>
</tr>
<tr>
<td>Canterbury Saleyards</td>
<td>60</td>
<td>17.97</td>
<td>demolition</td>
</tr>
<tr>
<td>Glassworks</td>
<td>50</td>
<td>15.27</td>
<td>demolition</td>
</tr>
<tr>
<td>Chch Women’s Hospital (plaque)</td>
<td>57</td>
<td>14.88</td>
<td>demolition</td>
</tr>
<tr>
<td>Chch Women’s Hospital (slab)</td>
<td>57</td>
<td>13.28</td>
<td>demolition</td>
</tr>
<tr>
<td>Turners &amp; Growers</td>
<td>50</td>
<td>12.41</td>
<td>demolition</td>
</tr>
<tr>
<td>Blenheim Rd Overpass</td>
<td>43</td>
<td>12.17</td>
<td>demolition</td>
</tr>
<tr>
<td>MPL 40mm</td>
<td>Mixed</td>
<td>12.14</td>
<td>crushed</td>
</tr>
<tr>
<td>MPL 20mm</td>
<td>Mixed</td>
<td>8.77</td>
<td>crushed</td>
</tr>
<tr>
<td>Concrete Recyclers 65mm</td>
<td>15</td>
<td>8.39</td>
<td>crushed</td>
</tr>
<tr>
<td>Concrete Recyclers Slab</td>
<td>15</td>
<td>8.22</td>
<td>demolition</td>
</tr>
<tr>
<td>Fulton Hogan 65mm</td>
<td>Mixed</td>
<td>6.91</td>
<td>crushed</td>
</tr>
<tr>
<td>Fulton Hogan 40mm</td>
<td>Mixed</td>
<td>6.12</td>
<td>crushed</td>
</tr>
<tr>
<td>Stevensons Masonry Block 2years</td>
<td>2</td>
<td>6.07</td>
<td>block</td>
</tr>
<tr>
<td>RM Core Sample 27/11</td>
<td>0.25</td>
<td>4.82</td>
<td>core</td>
</tr>
<tr>
<td>Allied</td>
<td>0.25</td>
<td>3.59</td>
<td>core</td>
</tr>
<tr>
<td>Stevensons Masonry Block 2Months</td>
<td>0.17</td>
<td>3.14</td>
<td>block</td>
</tr>
<tr>
<td>RM Core Sample 22/11</td>
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<td>3.34</td>
<td>core</td>
</tr>
<tr>
<td>Bombay Core Sample</td>
<td>0.1</td>
<td>0.63</td>
<td>core</td>
</tr>
</tbody>
</table>

### Figure 1: Carbonation Percentage versus Time

![Figure 1: Carbonation Percentage versus Time](image)
Photo 1: Core sample from Bombay Quarry which was less than two months old. The high colouration, and hence lack of carbonation, was consistent with the low carbonate percentage measured at 0.63%.

Photo 2: Cut sections of two masonry blocks obtained from the Stevenson block plant in Christchurch. The two year old block on the right can be seen to be more carbonated than the two month old block on the left.

Photo 3: Samples obtained from Fulton Hogan’s Pound Road Quarry in Christchurch. This material had been crushed and stockpiled for three years following its use in a recycled road project [9]. Two sizes of crushed concrete were sourced. The 40mm down gave a lower carbonate value of 6.12% than the 60mm down which had a value of 6.91%. The 40mm also contained concrete material which was purple in colour (top right of the photo).

Photo 4: Two samples from locations at the old Christchurch Woman’s Hospital. The plaque samples were obtained near the foundation plaque. This sample has a value of 14.88% carbonate. The steps sample had an anomalously high carbonate value of 24.79%. Later it was found that the step sample was composed of cement-rich mortar and as a result it was removed as an outlier when determining the line of best fit for Figure 1.

Photo 5: Crushed concrete stockpile from the Wallace Block in Auckland City Hospital. The sample was 84 years old (the oldest sample tested). The phenolphthalein test showed no purple colouration, while the carbonate titration value was 20.75%, indicating a high degree of carbonation. The material had been located in a stockpile for several months prior to sample collection.

CONCLUSION

Carbonation of concrete in a New Zealand context has been experimentally tested and has been determined to be a measurable phenomenon across a range of concrete types, ages and exposure conditions.

It is possible that the two oldest samples (from the Wallace Block and Canterbury Saleyards), which displayed high degrees of carbonation, have absorbed most, if not all, of the original
CO₂ produced from calcination during the cement manufacturing process.

While the extent of carbonation is affected by environmental and concrete composition parameters, the post-service demolition and crushing of concrete is considered to be an extremely significant factor in determining CO₂ uptake. The carbonation of concrete in New Zealand represents an important process which should be considered when discussing the embodied CO₂ of cement and concrete.

Further research is underway regarding the carbonation of crushed modern concrete compositions in a laboratory environment. The additional research is designed to help give a better understanding of the likely uptake of CO₂ from current concrete mix designs into the future.

With the wider use of crushed recycled concrete, the effects of carbonation must be considered in any rigorous life cycle assessment of the sustainability of concrete structures.

ACKNOWLEDGEMENTS

We are grateful to the many organisations and businesses that provided access to the wide range of samples required to conduct this research.

REFERENCES


