Fourth International Conference on Sustainable Construction Materials and Technologies http://www.claisse.info/Proceedings.htm



SCMT4 Las Vegas, USA, August 7-11, 2016

The Quantity of CO₂ Bound by Concrete Carbonation in Norway

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ABSTRACT

The binding of CO_2 by concrete carbonation is an on-going natural process. Many estimates have been given over the past decades and the last 5-10 year the knowledge has increased significantly regarding the capability to estimate the binding of CO_2 by concrete carbonation. This included better insight of the carbonation mechanisms, increased quantity of field data, and developments of models that calculate the CO_2 -binding by concrete in service life and in the recovery phase.

It was found that the Norwegian concrete stock in 2011 will bind around 165 000 tonnes assuming a service life and a recovery phase of 100 years each. Most of the CO_2 will be bound in service life, as the model calculated the binding to be 140 000 tonnes in this phase. Furthermore, it was found that the specific CO_2 -binding to cement was 111 kg CO_2 /ton of cement consumed, for which 94 kg CO_2 /ton of cement was bound in the service life of concrete. The model calculations were considered to be conservative to avoid overestimations.

Model prediction by further variation of the demolition rate demonstrated the strong influence of this parameter on the total CO_2 -binding in the recovery phase. If single products are demolished at 100% rate and at 90% crushing rate after service life, they may carbonate in the range of 69-93% by volume depending and the concrete quality.

INTRODUCTION

Carbonation of concrete normally occurs when air or water-borne CO_2 dissolves in the concrete pore water and react with Ca^{2+} to form stable $CaCO_3$ which is precipitated in the pore system. Upon carbonation, the pH of the concrete pore water is decreased to around 9. Although it is a well-known naturally occurring ageing process for concrete, the carbonation phenomena is quite complex as it involves a series of chemical reactions and physical processes. Thus, it is difficult to give a complete physico-chemical description of all processes involved. Carbonation mainly involves decalcification of the Ca-bearing hydrate phases when different polymorphs of CaCO₃ are formed. In addition, the Mg-bearing hydrate phases (OH-hydrotalcite and CO₃-hydrotalcite) will also carbonate by forming MgCO₃ and Al(OH)₃ when the hydrotalcite phases become unstable at pH less than 10. The former carbonation process is predominant since the average MgO content in Portland cement is less than 2 %. Carbonation is detrimental for concrete with steel reinforcement as the passive layer at the steel surface is broken at pH < 10, which means that the steel is no longer protected against corrosion. Therefore a minimum thickness of the concrete cover is defined for reinforced concrete. The minimum thickness depends on which exposure and structural class the concrete is classified under. In EN 1992-1-1:2004 the concrete thickness is defined in the range of 10-55 mm. Carbonation is in most cases not detrimental for concrete without reinforcement. In fact the carbonation process forms a denser concrete with increased compressive strength when precipitation of CaCO₃ occurs under normal temperature and CO₂ pressure encountered in the troposphere. Thus, for durability reasons of reinforced concrete, the carbonation speed is a critical factor. This normally relates to carbonation depth versus time and is usually measured by spraying phenolphthalein indicator on a fresh concrete surface. If the pH of concrete pore water is less than 10, this is indicated by a colorless surface and the carbonation depth can be assessed (indicator is pink for pH > 10). Thus, the phenolphthalein indicator is only providing information of where the carbonation front is located inwards the concrete relative to the boundary of pH 10. It follows from this that the CaO originally present is not necessarily fully converted to CaCO₃ in a carbonated area (indicated by phenolphthalein), since pH change made by carbonation is a gradient process. Likewise in the area of pH > 10 (pink), carbonation indeed takes place to a decreasing extent by increasing pH.

In the natural process of carbonation it is indisputable that CO_2 is bound to concrete and thereby reduces the net CO_2 footprint of cement and concrete. This environmental aspect has received significant attention lately, as CO_2 -binding by concrete is not included in any official environmental product declarations today. One of the first estimates on how much CO_2 that can be bound in concrete, due to carbonation, was carried out by Jahren [1998]. In this study, 5-25 % of the CO_2 released from cement production was anticipated to be bound globally in concrete during its service life as a result of carbonation. In a more systematic study, a CO_2 binding of 11 % was found Jacobsen and Jahren [2001]. A service life of only 20 years and a recovery phase where 10 % by mass of the annual Norwegian concrete production was converted to recycled aggregates for which the remaining depth was carbonated, were assumed. The early studies on CO_2 binding to concrete life cycle clearly showed that a significant amount of CO_2 is absorbed during concrete life cycle.

Since a number of parameters are controlling the carbonation process, the challenge is to provide more precise estimates that can be ascribed to for example a concrete strength class or an exposure scenario. This is also reflected in several studies conducted during the past 10 years (e.g. Talukdar et al 2012). In short, these studies focus on carbonation speed in various climatic conditions and for different concrete qualities, effect of the recovery phase and the carbonation degree (what is the available amount of CaO for carbonation). These are considered to be the major aspects that need to be dealt with in an adequately way in models that estimate the CO₂-binding in the service life of concrete as well as in the recovery phase. Recently, the CO₂-uptake in all existing Swedish concrete structures has been calculated by Andersson et al [2013]. They estimated that around 300 000 tonnes of CO₂ were bound to Swedish concrete structures in 2011, i.e. 17 % of the total emission from cement production in Sweden in 2011 is estimated to be bound to concrete due to carbonation. The authors calculated the accumulated CO₂ binding the last 100 years based on actual cement production data in the same time period. The estimated quantity bound in 2011 equals to 125 kg of CO₂ per tonne cement in Sweden.

The overall objective of the present study was to estimate the total CO_2 -binding for the Norwegian concrete stock. In addition, the study also aimed to estimate the CO_2 -binding in the recovery phase by model predictions at different demolition rates.

METHODS AND CALCULATIONS

Available CaO for carbonation. In order to estimate the normal CO_2 -binding capacity of cements, the quantity of the formed hydrate phases needs to be considered in addition to the chemistry during the

carbonation of each hydrate phase. Carbonation is basically degrading the C-S-H phase by incongruent dissolution¹. The C/S-ratio is decreased from around 1.5 to less than 0.75 by normal carbonation, i.e. when phenolphthalein indicator shifts from pink to colorless. The AFm/AFt phases will eventually decompose to aluminum and iron hydroxides, gypsum and calcium carbonate. The carbonation degree of the hydrate phases was assumed as follows:

- 100 % of CH carbonates (complete dissolution of CH);
- 50 % carbonation of C-S-H (de-calcification to a CaO/SiO₂-ratio of around 0.75);
- 75 % carbonation of AFm due to stoichiometry of calcium monosulfoaluminate $(C_4A\bar{S}H_{12})$ and the formation of gypsum in the carbonation process;
- 50 % AFt due to stoichiometry of ettringite ($C_6A\bar{S}_3H_{32}$) and the formation of gypsum in the carbonation process.

The phase contents in a hydrated Portland cement paste were assumed as follows:

- 25 % of CH
- 50 % of C-S-H
- 10 % of AFm
- 10 % of AFt

Based on the assumptions made above, the available CaO content for normal carbonation is calculated to be 72 % of the total CaO. Note that the presence of limestone powder in the cement (frequently used in CEM I) will change the phase assembly slightly. Calcium hemicarboaluminate ($C_4A\overline{C}_{0.5}H_{12}$) and ettringite will be the stable phases at small limestone powder addition (e.g. < 0.4 % as CaCO₃). At higher contents, monocarboaluminate ($C_4A\overline{C}H_{11}$) will be stable together with ettringite. These changes in the AFm phases will not affect the CaO available for carbonation significantly. It can also be mentioned that the presence of the iron analogues of AFm (e.g. $C_4F\overline{C}_{0.5}H_{12}$, $C_4F\overline{S}H_{12}$, etc.) will not change the CaO available for carbonation significantly as the stoichiometry is the same and the molar ratio is only slightly decreased provided that the thermodynamic stability is roughly the same.

Carbonation rate constant (*k-values*). The physical process of carbonation can mechanistically be described by the Fick's law of mass transport by diffusion. This is attributed to the fact that when the carbonation layer are formed during service life, the carbonate species need to penetrate through the denser carbonated layer which becomes thicker and thicker upon time and the carbonation rate slows down with the square root of time. By establishing diffusion coefficients, the carbonation depth can be predicted for a defined service life of concrete. Empirical diffusion coefficients (or rate constants) are typically established by determining the carbonation depth in a concrete with a known age. Many field studies have been conducted and characteristic rate constants have been systemized based on the concrete qualities [Engelsen and Justnes 2014].

Fick's first law applies to steady-state diffusion in one dimension with mass transport over a concentration gradient. In reality the driving force is the chemical potential. However, the concentration gradient is usually changing in time and space and Fick's second law may be applied according to Equation (1):

$$\partial c / \partial t = D \left(\partial^2 c / \partial x^2 \right) \tag{1}$$

¹ Cement chemistry notation: C = CaO; $S = SiO_2$; $A = Al_2O_3$; $F = Fe_2O_3$; $AFm = Aluminoferrite mono-substituted; AFt = Aluminoferrite tri-substituted; <math>H = H_2O$; $\overline{S} = SO_3$ $\overline{C} = CO_2$

where c = concentration, t = time, x = surface area and D = diffusion coefficient.

In general, the diffusion coefficient is proportional with the squared particle velocity which is influenced by temperature, viscosity and size of particles. Fick's second law express how the concentration changes with time $(\partial c / \partial t)$ due to the diffusion process. Applying Equation (1) to describe the carbonation process in concrete system, the diffusion coefficient *D* will be dependent on the connective porosity as the main material parameter. In addition, both gas and liquid transport need to be described which complicates the solution of the differential equation.

One way to simplify is to describe the carbonation depth versus time. This requires empirically obtained diffusion coefficients for specific concrete types and environments. By systemising the observed diffusivity for the most typical exposure conditions with the most conventional concrete types, model predictions of depth can be made by the following equation:

$$d_c = k \cdot \sqrt{t} \tag{2}$$

where $d_c = carbonation \ depth \ (mm), \ k = rate \ diffusion \ coefficient \ (\frac{mm}{\sqrt{vear}}), \ t = exposure \ time \ (year).$

It follows from Equation (2) that by measuring carbonation depth and the exposure time, the rate coefficient k can be estimated.

Calculation of total CO₂-binding. By considering the CO₂-binding capacities (derived from the available CaO for carbonation) for the commonly used cements in Norway, the carbonation degree and the carbonation rate, the total CO₂ bound to Norwegian concrete volume was estimated. To be able to conduct such calculations, the relevant distribution of ready-mixed concrete (RMC), precast element concrete (PEC) and precast concrete product (PCP) in the different concrete segments was found. Furthermore, this distribution was coupled to the main scenarios as shown in Table 1. The procedure for the calculations consisted of the following steps:

- The concrete volume for each segment and in each scenario in Table 1 was estimated; the average thickness was also estimated.
- Annual cement and concrete consumption and estimated distribution into the concrete segments.
- Calculation of the total exposed surface area.
- The carbonated volumes were calculated by multiplying the surface area with the carbonation depths using the k-values estimated for the main scenarios.
- The service life chosen was 100 years.
- Recovery phase was chosen to be 100 years.

Details and input data (e.g. *k*-values) used in the model are provided in [Engelsen and Justnes 2014]. The output of the model was the total quantity of CO_2 bound by concrete consumed in Norway in 2011 assuming an onward service life of 100 years. Note that in the previous Swedish study [Andersson et al 2013], they also calculated the CO_2 binding 100 years backwards, i.e. binding that already have taken place, in addition to 50 years onward service life (80 years in total). Comparing the data between Norway and Sweden should therefore be conducted carefully. It should also be emphasised that the effect of the blended cements used in Norway was included in the present model.

For the carbonation in the recovery phase the carbonated concrete volume in service life was subtracted from the annual total volume. Part of the remaining carbonation free volume was transformed to spherical particles with at different particle sizes (<1 mm, 1/10 mm, 10/30 mm and > 30 mm). The CO₂-binding was then conducted by the carbonation model using the corresponding *k*-values used in service life considering the main scenarios used for crushed concrete.

Table 1. Ready-mixed concrete (RMC), precast element concrete (PEC) and precast concrete product (PCP) relevant in the main scenarios and for the different concrete segments

Concrete segment	Main scenario ¹					
	Indoor	Indoor painted	Indoor other coverings	Outdoor sheltered	Outdoor naked	Buried
Walls	RMC	RMC	RMC	RMC	RMC	n.a.
Slabs	RMC	RMC	n.a.	RMC	RMC	n.a.
Foundations	n.a.	n.a.	n.a.	n.a.	n.a.	RMC
Structures	n.a.	n.a.	n.a.	RMC	RMC	RMC
Sleepers	n.a.	n.a.	n.a.	n.a.	PEC	PEC
Hollow core slab total	PEC	PEC	PEC	n.a.	n.a.	n.a.
Formwork elements	PEC	PEC	PEC	n.a.	n.a.	n.a.
DT elements: floors, roof, etc.	PEC	PEC	PEC	n.a.	n.a.	n.a.
Isolated wall	PEC	PEC	n.a.	PEC	PEC	n.a.
Con form wall	PEC	PEC	n.a.	PEC	PEC	n.a.
Wall elements	PEC	PEC	n.a.	n.a.	n.a.	n.a.
Columns	PEC	PEC	n.a.	n.a.	n.a.	n.a.
Beams	PEC	PEC	n.a.	n.a.	n.a.	n.a.
Stairs	PEC	PEC	n.a.	n.a.	n.a.	n.a.
Bridges, quays, culverts	n.a.	n.a.	n.a.	n.a.	PEC	PEC
Concrete paving	n.a.	n.a.	n.a.	n.a.	РСР	n.a.
Pavement block	n.a.	n.a.	n.a.	n.a.	n.a.	PCP
Retaining Wall	n.a.	n.a.	n.a.	n.a.	РСР	n.a.
Curbstone	n.a.	n.a.	n.a.	n.a.	РСР	PCP
Block products	n.a.	n.a.	n.a.	n.a.	РСР	PCP
Pipes	n.a.	n.a.	n.a.	n.a.	n.a.	PCP
Shafts	n.a.	n.a.	n.a.	n.a.	РСР	PCP
Roof tiles	n.a.	n.a.	n.a.	РСР	РСР	n.a.

 1 *n.a* = *not applied*

RESULTS AND DISCUSSIONS

CO₂-binding capacity of cement. In 1000 kg Portland cement that consists of 95 % clinker, 617 kg of CaO can theoretically be converted to CaCO₃ by consuming CO₂ from the air (in further calculations 600 kg of CaO was used). Thus, the theoretical CO₂-binding capacity in Portland cement is 471 kg CO₂/ton. In order to be able to estimate the CO₂-binding by concrete, the normal binding capacity was calculated. This corresponded to a carbonation degree equal to ~70 % conversion of total CaO to CaCO₃, as shown above. The calculated binding capacities for the commonly used cements in Norway are shown in Table 2.

Cement type	Fly ash (%)	Slag (%)	CO ₂ -binding capacity (kg/t)
CEM I	Not applicable	Not applicable	330
CEM II/A-V ¹	20	Not applicable	255
CEM II/B-S ²	-	33	294

Table 2. CO₂-binding capacities for normal and blended cements

¹ Siliceous fly ash with a glass content of 65% consisting of 35% SiO₂ and 15% Al₂O₃ and where 80% of the glass phase has reacted over time, the consumption of calcium hydroxide per gram fly ash; 0.80 x 0.65 x 0.35 x 1 x $M_{Ca(OH)2}/M_{SiO2} = 0.22$ g to form C-S-H of C/S = 1 not available for carbonation; 0.80 x 0.65 x 0.15 x 3 x $M_{Ca(OH)2}/M_{Al2O3} = 0.17$ g to form C₃AH₆ presumably available for carbonation [Fernàndez-Carrasco et al 2012].

² Blast furnace slag with composition of 40 % CaO, 9 % MgO, 11 % Al₂O₃ and 40 % SiO₂. 70 % of the CaO in the slag was assumed to be able to carbonate.

Cement and concrete consumption in Norway. The net consumption of the specific cement types is given in Table 3. It can be seen that around 50 % of the consumed cements is Portland-fly ash cement.

X.	Norwegian	Imported	Exported	Net	Net consumption of cement types		ment types
Year	cement production			consumption	CEM I	CEM II/A-V	CEM II/B-S
2011	1.547	0.371	0.094	1.824	0.650	0.988	0.186
2012	1.698	0.400	0.150	1.948	0.695	1.053	0.200

Table 3. Norwegian production and net consumption of cement (in mill. tons)

The total concrete consumption in Norway in 2011 was 4.5 million m³ concrete. This corresponds to 10.6 million tonnes of concrete. The total concrete consumption was calculated from production data given for the concrete sub segments (e.g. hollow slab concrete, formwork elements, etc.) in addition to the imported concrete. It can be noted that the annual concrete rubble generation in Norway was around 0.75 million tons [Statistics Norway 2014], i.e. less than 10 % of the concrete consumed in construction.

Maximum binding. To quantify the maximum CO_2 binding by concrete in Norway, the calculated binding capacities (Table 2) were used in conjunction with the Norwegian consumption of different cement types. The maximum binding was calculated to be around 550 000 tonnes of CO_2 as shown in Table 4, if the whole concrete volume was carbonated. Note that this number is not the theoretical capacity which is higher. The maximum binding showed the potential of CO_2 -binding considering the normal carbonation degree.

		100.0/		
Table 4 Maximum	hinding of CO ₂ b	v 100 % carb	onation based on	cement consumption
I abic 4. Maximum	0 multiply of 0.02 c	y 100 /0 cui b	onation based on	content consumption

		CO ₂ binding (to	Total (tons)	
Year	CEM I	CEM II/A-V	CEM II/B-S	
2011	215 000	252 000	55 000	521 000
2012	229 000	268 000	59 000	557 000

Actual binding. The total CO_2 -binding for all concrete qualities and segments is given in Table 5. It can be seen that a significant quantity of CO_2 is bound to concrete life-cycle. It is interesting to see that the modelling showed that the binding during service life was calculated to be 94 kg CO_2 /ton cement consumed. Considering a recovery phase with conservative assumptions, the total binding was found to be 111 kg

 CO_2 /ton cement consumed. Considering the share of blended cements consumed on the Norwegian market, the total CO_2 emission is around 700 kg CO_2 /ton cement produced. Hence, around 15 % of the emission is bound during the life cycle of concrete.

Table 5. Total CO2 bound to Norwegian concrete in 2011 assuming 100 years of service lifeand 100 years of recovery phase

Stage	Exposure (Years)	Total binding (ton CO ₂)	Average binding kg CO ₂ / ton cement
Service life	100	140255	94
Recovery phase	100	25152	17
Total	200	165407	111

A comparison with the Swedish study [Andersson et al 2013] should be conducted with care since a different approach was used. They calculated that 300 000 tonnes of CO_2 was bound to Swedish concrete in 2011 based on historical cement consumption the last 100 years. This corresponded to 125 kg CO_2 /ton cement consumed. The historical cement consumption in Norway was significantly smaller and the same model calculation based on historical data will give a smaller amount of total CO_2 -binding than in Sweden.

The differences in CO_2 bound per unit mass of cement were due to the blended cement share used in the Norwegian calculations. The binding capacity was reduced from 330 kg CO_2 /ton of CEM I to 255 kg CO_2 /ton of CEM II/A-V and 294 kg CO_2 /ton of CEM II/B-S. There were also differences in some of the calculated *k*-values used in the Swedish study which is most likely adequate since a more sophisticated model was used by them. Considering these factors, the calculated CO_2 -binding per unit cement in Norway was comparable to the CO_2 -binding in Sweden.

CO₂-binding in the recovery phase by increased demolition rate. It was shown in Table 5 that only 15% of the total CO₂-binding occurred in the recovery phase. This is based on the following assumptions: 10% of the concrete volume consumed annually was demolished within the recovery phase (demolition rate) and 90% of this volume was crushed (crushing rate) within the recovery phase. It means that 10% of the consumed concrete volume will be demolished after 100 years of service life on average. For some concrete product groups this may not be the case because demolition and crushing may occur at a higher rate. Roof tiles and certain concrete elements are product groups were nearly100% may be demolished after service life. Thus, the total CO₂-binding was calculated assuming 50% and 100% demolition rates using the same model. The calculations are shown separately for RMC, PCP and PEC in Fig. 1 and it can be seen that the demolition rate is a critical parameter. By increasing the demolition rate from 10% to 50%, the total carbonated volume increased in the range of 41-64%, 32-48% and 34-59% for RMC, PCP and PEC, respectively. It can also be seen that the lowest carbonated volume was obtained by PCP due to the high concrete quality used in this segment. In addition, single products demolished at 100% rate after service life, may carbonate in the range of 69-93% by volume depending and the concrete segment. It is emphasised that the crushing rate have been held at a constant level of 90% in all calculations. The crushing rate is obviously also a crucial parameter and research is underway to estimate this parameter more precisely.



Figure 1. Carbonated volume as function of exposure time and demolition rate for (a) RMC, (b) PCP and (c) PEC. Horizontal red line represents the total volume of concrete consumed in 2011.

CONCLUSION

The binding of CO_2 by concrete carbonation is an on-going natural process. Many estimates have been given over the past decades and the last 5-10 year the knowledge has increased significantly regarding the capability to estimate the binding of CO_2 by concrete carbonation. This included better insight of the carbonation mechanisms, increased quantity of field data, and developments of models that calculate the CO_2 -binding by concrete in service life and in the recovery phase. As more field data will be available, model modification can easily be conducted to still improve the prediction of CO_2 -binding by concrete *k*-values.

In the present study, the CO_2 -binding capacities for the cement types consumed in Norway was used to calculate the total binding of CO_2 by the Norwegian concrete stock. It was found that the Norwegian concrete stock built in 2011 will bind around 165 000 tonnes CO_2 assuming a service life and a recovery phase of 100 years each. Most of the CO_2 will be bound in service life, as the model calculated the binding to be 140 000 tonnes in this phase. Furthermore, it was found that the specific CO_2 -binding to cement was 111 kg CO_2 /ton of cement consumed, for which 94 kg CO_2 /ton of cement was bound in the service life of concrete. The model calculations were considered to be conservative in order to avoid an overestimation. The calculated CO_2 -binding per unit cement in Norway can be regarded to be roughly in the same range as the CO_2 -binding in Sweden.

Model prediction by further variation of the demolition rate demonstrated the strong influence of this parameter on the total CO_2 -binding in the recovery phase. If single products are demolished at 100% rate and at 90% crushing rate after service life, they may carbonate in the range of 69-93% by volume depending and the concrete segment.

ACKNOWLEDGEMENTS

The Environmental committee of Norwegian Concrete Association is acknowledged for their valuable input and support to the study.

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