

BJÖRN LAGERBLAD

This is the cover for a CBI report (backside to the left and this is the front side). All our reports in this serie have the same lay-out.

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Carbon dioxide uptake during concrete life cycle – State of the art

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Preface

The objective of this project, of which this report is a part, is to provide documentation of concrete carbonation during service life and secondary use. This documentation should be used for environmental assessment of concrete buildings and structures, and to evaluate the effect of concrete carbonation on the overall CO₂ emissions from cement and concrete production in the Nordic countries.

Approximately half of the CO₂ emission from cement production stems from the calcination of limestone, i.e. a process where limestone is burnt and CO₂ gas is released to the atmosphere. Theoretically, hardened concrete binds approximately the same amount of CO₂ in a process called carbonation. The concrete's ability to bind CO₂ and the rate of the process depends on many variables, including the type of concrete and its application.

The methodology and the impact that concrete carbonation has in the assessment of CO₂ emissions from concrete has not been fully documented. Specifically, there is a lack of knowledge about the carbonation of demolished and crushed concrete. The existing models for calculating carbonation do not take into account that the concrete is crushed and recycled after use. Consequently, the contribution of the cement and concrete industry to net CO₂ emissions is strongly overestimated. This overestimation has a significant influence on CO₂ policy; on the criteria for environmental labelling; and on the selection of materials based on principles of environmentally correct design. A comparison of the environmental impacts from different building materials (e.g. concrete versus wood and steel) is at present unfair because of the lack of documentation of the CO₂ uptake in concrete.

The present report is one of five documents published during the project "CO₂ uptake during the concrete life cycle". Three reports cover the background data and the last two reports include the results of the project.

The background reports are:

- Carbon dioxide uptake during concrete life cycle, state of the art, published by Swedish Cement and Concrete Research Institute (CBI), www.cbi.se, ISBN 91-976070-0-2.
- Information on the use of concrete in Denmark, Sweden, Norway and Iceland, published by Icelandic Building Research Institute, www.ibri.is, ISBN 9979-9174-7-4.
- Carbon dioxide uptake in demolished and crushed concrete, published by Norwegian Building Research Institute, www.byggorsk.no, ISBN 82-536-0900-0.

The reports with results are:

- Guidelines – Uptake of carbon dioxide in the life cycle inventory of concrete, published by Danish Technological Institute, www.teknologisk.dk, ISBN 87-7756-757-9.
- The CO₂ balance of concrete in a life cycle perspective, published by Danish Technological Institute, www.teknologisk.dk, ISBN 87-7756-758-7.

The participants in the project are:
Danish Technological Institute (Project Manager)
Aalborg Portland A/S (Head of Steering Committee)
Norwegian Building Research Institute
Norcem A.S
Elkem ASA Materials
Cementa AB
Swedish Cement and Concrete Research Institute
Icelandic Building Research Institute

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Summary

Carbonation results when carbonate ions from dissolved carbon dioxide react with the Ca ions of the cement paste and precipitate calcium carbonate. By time all Ca-bearing cement hydrates will decompose and form calcite. The end product will apart from calcite be silica gels, metal hydroxides and clays. Carbon dioxide and water can be found in almost every environment and thus all concretes will be subjected to carbonation. The cement paste will in the course of time go back to the basic components in cement production. Therefore, the question is not if concrete and other cementitious products will carbonate, but how fast they will carbonate. In geological terms the cement paste turns into marly limestone and the concrete into marly agglomerate. Old Roman concrete structures are basically such a rock.

Carbonation is a process from the surface, i.e. the amount of carbonated material is related to exposure time and surface. Surfaces in direct contact with carbon dioxide and water will carbonate rapidly but a shell of already carbonated concrete will slow down the carbonation of the interior. Thus to be able to calculate the CO₂-uptake we must know the transport mechanism of carbon dioxide and carbonate ions through the already altered product. The process of passing a shell of already carbonated concrete is complex. The speed of carbonation is apart from the amount of CO₂ in the environment also governed by the size and geometry of the porosity, the degree of water saturation, the type of cement/binder, the temperature, etc. Even concrete submerged in water or buried in soil will carbonate but at a slow speed due to biological degradation and the slowness of exchange reactions between water and the gases in the atmosphere.

To be able to calculate CO₂ uptake one must consider the microclimate at individual concrete surfaces, concrete qualities and cement/binder types in a time frame. Thus approximations are needed. In the general case assuming a similar environment and concrete quality the carbonation rate slows down with the square root of time. By choosing the most common types of concrete structures, estimating the exposed surfaces in different environments and concrete qualities it is possible to get a good estimate of the rate of carbon dioxide uptake.

As a consequence of the rapidly decreasing rate of carbonation one can assume that most of the carbonation of concrete structures takes place during the first 50 years and after demolition as this will increase the surfaces dramatically. One must, however, also consider that the types of cement and quality of the concrete have changed and will change over time. Thus there will be a difference between how much is taken up today and how much that will be taken up in 50 years from now. Concrete is a fairly modern material and most concrete structures still remain but we can expect the amount of demolished concrete to increase in the future. A guess is that a 100-year perspective most concrete structures that exist today will probably be demolished and most of the carbonate rock calcinated during cement production will be back as a carbonate rock.

To be able to calculate the carbonation rate some simplifications are needed. In this report concrete strength is used as a substitute for porosity and from literature data constants for different environmental classes are selected. The influence of different cements and additions is handled by correction factors.

Sammanfattning

Denna rapport är en del i ett större forskningsprojekt med syfte att dokumentera betongkonstruktioners karbonatisering både under drift och efter rivning. Ändamålet är att få in karbonatiseringen i ett större miljösammanhang, att få ett bättre underlag för att utvärdera cementtillverkningens effekt på halterna av koldioxid i atmosfären i ett längre tidsperspektiv. Denna rapport avser att ge information om aktuellt kunskapsläge och underlag för de andra delprojekten.

Karbonatisering är ett resultat av att koldioxid i fuktig miljö reagerar med kalciumjoner i cementpastan och bildar kalciumkarbonat. Denna omvandling resulterar i att den kemiska miljön i cementpastan förändras så att pH-värdet sjunker vilket gör att även alla andra hydratfaser blir instabila, bryts ner och bildar olika typer av silikageler, metallhydroxider och/eller lermineral. I en längre tidsskala kommer cementpastan att återgå till ett material liknande det ursprungliga råmaterialet vid cementtillverkningen. Med geologiska termer kommer cementpastan att övergå till en mörk kalksten, betongen till ett mörkt agglomerat. Den gamla romerska betongen är en sådan omvandlingsprodukt idag.

Karbonatisering är en process som sker från ytan och inåt, dvs. mängden karbonatiskt material står i relation till den exponerade yta som är i kontakt med den yttre miljön. Ytor i kontakt med koldioxid och vatten kommer att reagera snabbt men det skal av karbonatprodukter som bildas kommer att minska karboniseringshastigheten. För att kunna beräkna mängden karbonatiskt material måste man därför förstå hur koldioxid/karbonatjoner transporteras genom redan karbonatiserad cementpasta. Denna transportmekanism som involverar både gas och jondiffusion är komplex men i princip minskar karboniseringshastigheten med tjockleken på den omvandlade produkten. Andra styrande parametrar förutom halten koldioxid i luften är storlek och geometri i porsystemet, typ av cement/bindemedel, temperatur, etc. Även dränkt i vatten utan direktförbindelse med atmosfären kommer betong att karbonatisera men i långsammare takt. Därför måste man kunna göra en bedömning av karboniseringshastighet för olika betong i olika miljöer med hänsyn tagen till yta och tid. Principiellt minskar karboniseringshastigheten med övriga parameter konstanta med kvadratroten ur tiden

För att kunna beräkna koldioxidupptaget måste man beakta mikromiljön för individuella betongytor, betongkvalitet och bindemedelstyper i en tidsskala. Man kan generellt anta att den största delen av karbonatiseringen sker under de första femtio åren och efter rivning då denna ökar ytan och därmed karboniseringshastigheten kraftigt. Man måste emellertid även beakta de förändringar som skett och kommer att ske med både bindemedel och betongkvalitén. Betong är ett relativt modernt byggmaterial och det mesta befinner sig fortfarande i konstruktion men vi kan anta att mängden rivningsmaterial kommer att öka framöver. I ett hundraårsperspektiv kan man förmoda att de flesta befintliga betongkonstruktioner kommer att vara rivna och det mesta av cementpastan kommer att vara karbonatiserad. Detta medför att största delen av den i cementproduktion kalcinerade kalkstenen kommer att ha återgått till kalksten.

För att beräkna karboniseringshastigheten är förenklingar nödvändiga. För beräkningarna används betongstyrkan som substitut för porositet. Karboniseringshastigheter för olika kvaliteter och miljöer är uppskattade från litteratordata. Påverkan av olika typer av cement och tillsatsmaterial behandlas med hjälp av korrektionsfaktorer.

1 Introduction

To find the CO_2 uptake we must know the amount of Portland cement in concrete structures and the amount of this cement that has been carbonated. Carbonation is an environmental process in time. Thus to make an accurate calculation we must know the carbonation process and put it in a temporal context.

The carbonation process is in theory very simple but in reality complex. Basically calcium hydroxide (CaOH) in contact with carbon dioxide (CO_2) forms calcium carbonate (CaCO_3). Water is not consumed but is needed in the transformation. When the CH is consumed the pH of the cement paste/pore solution will drop and all the other hydrate phases will successively break down. The final product will consist of a mixture of carbonates together with ferrite, silicate and aluminium-hydroxide phases. The major challenge is not the chemistry of alteration but the kinetics and speed of the carbonation process.

Carbon dioxide is a gas in the atmosphere and form bicarbonate and/or carbonate ion in water together with some dissolved carbon dioxide gas. Carbon dioxide gas and carbonate ions can be found almost every environment on the surface of earth. The problem is thus mainly the accessibility and mode of entering the concrete. Thus, the rate of carbonation varies considerably and thus the CO_2 uptake will depend on both the type of concrete and the environment in which the concrete is placed.

Carbonation is a reaction where carbon dioxide gas or carbonate ions must pass through a carbonated surface into the material to reach fresh concrete. This is a diffusion process either by carbon dioxide gas or by carbonate ions, which in turn is controlled by the water saturation of the capillary system. The carbonation will slow down as the carbon dioxide must pass through a thickening layer of its alteration products. The speed of transport is mainly governed by concentration gradients, transport media (porosity) and thickness of the already carbonated concrete. Thus we must know not only the properties of concrete but the effect of alteration on the connective porosity. Thus to understand the extent and amount of carbonation one must differentiate between different environments and different details and different types of concrete. The dominant factors and concrete environments must be recognised, quantified and calculated.

To be able to calculate CO_2 -uptake over time perspective we must also consider the lifetime of the different concrete details. Generally, carbonated concrete is hard and stable and carbonation will thus not endanger the stability of the concrete. Most concrete structures, however, contain reinforcement that may rust when the concrete is carbonated. Thus most concrete structures have a lifetime. Buildings are normally designed to have a lifetime of 50 years while civil engineering structures are designed to have a lifetime of 100 years. In most cases, however, the real lifetime is longer due to patch repair etc, but one can expect that most buildings will be demolished within 100 years. Moreover there are considerable volumes of concrete that are demolished before the estimated lifetime. When concrete is demolished and crushed it will carbonate faster due to the much larger exposed surface.

When calculating CO_2 uptake we must consider the amount of Portland cement clinker used over time and a prediction of the amount that will be used in the future. We must also know the concrete types and quality, the amount of different types of concrete in the different environments. In all cases we need to know the area of the exposed surfaces.

2 Chemistry of carbonation

Carbonation is due to the fact that in the presence of carbonate ions the calcium ions in the pore solution precipitate and form calcium carbonate. Calcium carbonate has a very low solubility. In concrete this will result in all Ca compounds dissolving and finally forming calcium carbonate. A model for the description of the reactions can be found in Bary & Sellier (2004).

The atmosphere contains substantial amounts of carbon dioxide. Gaseous CO₂ cannot, however, react directly with the hydrates of the cement paste. Thus the CO₂ gas must first dissolve in water and form carbonate ions that in turn will react with the Ca ions of the pore water. Carbon dioxide will dissolve in water. The type of carbonate ions depends on the pH. When CO₂ comes into contact with water at neutrality it forms bicarbonate. Inside concrete, the pH is high and as a result the bicarbonate dissociates and forms carbonate ions. Thus in the carbonated layer bicarbonate forms but closer to the uncarbonated cement paste this carbonate ions form (due to higher pH) and precipitate calcium carbonate crystals (CC). Calcium carbonate exists in three crystallographic forms, aragonite, vaterite and calcite. Calcite and vaterite are commonly found in carbonated concrete. Presumably the metastable vaterite will transform into stable calcite over time.

The carbonation process can be described by the following chemical equations;

1. $\text{CO}_2 (\text{g}) + \text{H}_2\text{O} = \text{HCO}_3^- (\text{bicarbonate ion}) + \text{H}^+$
2. $\text{HCO}_3^- = \text{CO}_3^{2-} (\text{carbonate ion}) + \text{H}^+$

The carbonate ion will react with Ca ions in the pore solution.

3. $\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3$

This will lead to lower concentration of Ca²⁺ which in turn will lead to dissolution of primarily calcium hydroxide (CH). The solubility of CC is much lower than that of CH.

4. $\text{Ca}(\text{OH})_2 = \text{Ca}^{2+} + 2 \text{OH}^- (\text{solubility } 9.95 \times 10^{-4})$
5. $\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3 (\text{solubility } 0.99 \times 10^{-8})$

Thus Ca(OH)₂ (CH) will dissolve and CaCO₃ (CC) will precipitate and the process will continue until all of the CH is consumed. Apart from CH the cement paste contains calcium silicate hydrate (C-S-H) and ettringite/monosulphate (AFt/AFm). These components are in equilibrium with and stabilised by high pH and Ca ions in the pore solution. Thus when the CH is consumed the pH and the Ca ion concentration drops and the C-S-H will dissolve congruently. Monosulphate (AFm) will decompose at a pH of around 11.6 and later the ettringite (Aft) will decompose at a pH of around 10.6. At pH < 9.2 (when the phenolphthalein change colour) none of the original Ca containing phases remain. Most of the Ca from the C-S-H will be bound to calcium carbonate but some Ca will always remain in silica gel.

The most complicated transformation is that of the main cement paste phase C-S-H. It is built up of short silica chains bound together by Ca²⁺ and OH⁻ ions. When the carbonation lowers

the content of Ca^{2+} in the pore solution this will be compensated for by the release of Ca^{2+} from C-S-H. This will successively change the composition of the C-S-H and give it a lower Ca/Si ratio. Eventually when the Ca/Si ratio drops to less than 1 (Stronach & Glaser 1997) and the pH is around 10 it will transform into a silica gel. However, always some Ca will always remain in the silica gel. Bary and Sellier (2004) assume that the remaining C-S-H in the fully carbonated zone has a CaO/SiO_2 ratio of 0.85 compared to 1.65 in the uncarbonated zone. This can be described by the following equation that mainly tells us that during the chemical reaction the C-S-H releases CH which is carbonated and that this process gives a C-S-H with lower contents of CaO.

6. $\text{C-S-H (1)} = \text{C-S-H (2)} + \text{CH}$ where $\text{Ca/Si (2)} < \text{Ca/Si (1)}$

Both ettringite and monosulphate are stabilised by high pH and high concentrations of Ca-ions. Gabrilová et al. (1991) found that in non-equilibrium conditions the disappearance is related to pH.

At around a pH of 11.6 the AFm (monosulphate) will decompose into ettringite and aluminate compounds. At around 10.5 AFt (ettringite) will decompose resulting in sulphate ions and aluminium hydroxide compounds.

The released sulphate ions will either precipitate as gypsum or diffuse inwards and react with aluminate ions from decomposed monosulphate and form new ettringite. This phenomenon is due to decreasing pH and can be observed in leached cement paste (Lagerblad 2001) and carbonation will give the same. The end result is that most of the Ca-ions from the aluminate phases will form carbonate and that the aluminate and ferrite phases will form stable metal hydroxides (Fig. 2).

The pore solution is dominated by alkali ions that will suppress the solubility of Ca^{2+} ions but still the CH will dissolve and CC will precipitate. When the paste has carbonated the pH will drop and bicarbonate ions will be stable. This is an acid and thus silica gel at a pH close to neutral will be the stable compound. Thus one will also get a front where bicarbonate converts to carbonate ions.

To be able to calculate the CO_2 uptake we must know how much Ca that remains in the carbonated concrete. In most cases (and for practical reasons) the carbonation depth is determined by phenolphthalein. It loses its colour when pH is less than 10, which corresponds to a CaO/SiO_2 of less than 0.8 (Chen et al 2004). Taylor (1997) has estimated that in cement paste with 65.3 wt % CaO 31.4 wt % is bound to C-S-H. All CH will form CC, most of the CaO of the C-S-H will form CC and the AFm and the AFt will decomposed. If we assume that all CaO in the CH, half of the CaO in the C-S-H (see above) and half of the CaO of the AFm/AFt are transformed to CC, around 24 % of the CaO of the original cement remain uncarbonated. This also assumes that all of the remaining unhydrated cement grains have reacted and are carbonated.

In concrete with pozzolanas like fly ash and silica fume the ratio will be somewhat less as there will be relatively more C-S-H in the cement paste and thus relatively more Ca in the remaining silica gel. In a geological time perspective pure silica gel will crystallize and most of the Ca will probably go to carbonate phases.

Table 1. Phase changes in the carbonation process. The CH, AFm and AFt will act as buffer phases and will be decomposed. The C-S-H will release CH, which carbonates resulting in a lower Ca/Si ratio, which is linked to a lower pH (Chen et al 2004).

Intact concrete	First stage	Second stage	Third stage	Carbonated
CH	-----	-----	-----	-----
C-S-H (1)	C-S-H (1)	C-S-H (2)	C-S-H (3)	SH (with some CaO)
	CC	CC	CC	CC
AFm	AFm	Aft/ Al(OH) ₃	Al(OH) ₃	Al(OH) ₃
AFt	AFt	AFt	Fe(OH) ₃	Fe(OH) ₃
pH >12,5	pH < 12,5	pH < 11.6	pH <10.5	pH < 10

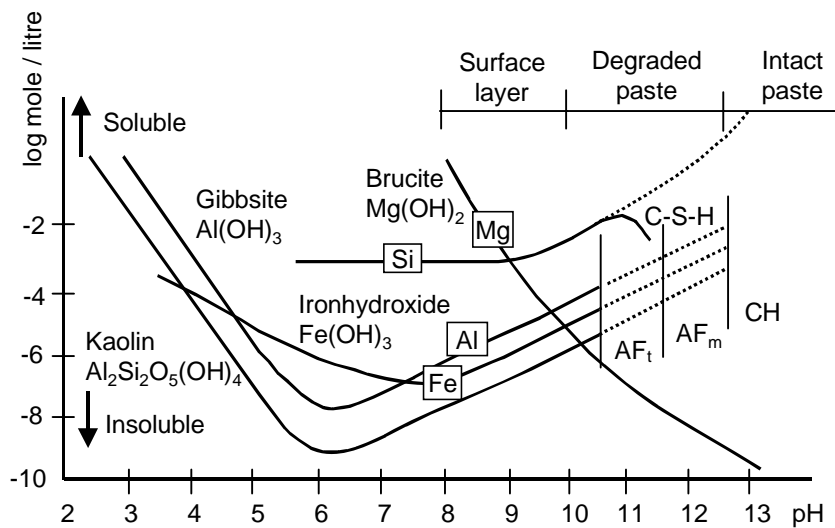


Figure 1. Solubility of cement paste and different metal hydroxides at decreasing pH. From Lagerblad 2001.

3 Mechanism of carbonation

3.1 Carbonation of concrete subjected to air with CO₂

The reaction mechanism is important, as it will control the structural changes in the carbonated shell. The effect will depend on the proportion between the different phases in the cement paste, which in turn depend on the binder type, curing and water-binder ratio. Pozzolanas will decrease the amount of CH and increase the amount of C-S-H. Granulated blast furnace slag (GBFS) changes the composition of the hydrates, lowers the Ca/Si ratio of the C-S-H and gives less CH (Taylor 1997). The amount of CH and the composition of the C-S-H depend on the amount of pozzolanas or GBFS.

The mechanisms of carbonation that will occur in the water phase depend on the solubility and speed of diffusion. Diffusion is controlled by concentration differences. Thus we must consider the diffusion processes and the effect on the structure of the carbonated layer. It is a process with inward diffusion of carbon dioxide gas and carbonate ions. Gas diffusion is much faster than ion diffusion. Thus the speed of carbonation depends on the humidity in the concrete, i.e. how filled with liquid the connective pore system is. In dry concrete the carbon dioxide can penetrate deeply but there is not enough water for the carbonation reaction. In fully water saturated concrete only carbonate ions can move and carbonation is slow. Thus there is an optimum where the speed of carbonations is at maximal. Where this optimum is depends on the porosity of the carbonated layer, how the water blockade gas diffusion. More porous concrete seems to have an optimum at a higher degree of water saturation than more dense concrete. In general a low water/binder ratio of the concrete gives a more dense alteration product, which in turn gives a slow carbonation rate.

It is, however, a two-way diffusion. The carbonation process will lower the content of Ca²⁺ ions in the pore solution, which in turn will trigger dissolution of CH and Ca²⁺ diffusion from the interior of the concrete to the carbonation front where the concentration of both components will be at a low point due to the low solubility of calcium carbonate (CC). The point of CC precipitation depends on the concentration gradient of both components. This will influence the structure and porosity of the carbonated layer. In the extreme case of carbonation of concrete submerged in stagnant water the low concentration gradient of and speed of diffusion of carbonate ions relative to diffusion of Ca²⁺ ions from the interior will result in the precipitation of calcite at and densification of the concrete surface (Lagerblad 2001). A consequence of this is that a high content of CO₂-gas, like in many accelerated tests, will give false results as the speed of diffusion of carbonate ions will be larger and the precipitation will not occur at the same place as in normal environments and thus the effect on the porosity will be different.

Carbonation gives rise to volume changes. Transformation of CH to calcite gives a volume change of 11 % and to the metastable vaterite 14 %. The volume change in the transformation of the C-S-H is, however, more uncertain and will depend on the water content of the silica gel. The volume changes will affect the porosity in the carbonated layer and thus the speed of diffusion. We know that the volume changes do not affect the mechanical stability of the carbonated layer, it is stable and hard. This indicates that, normally, the surplus volume of calcite precipitation mainly fills empty space in the capillary system and thus densifies the cement paste.

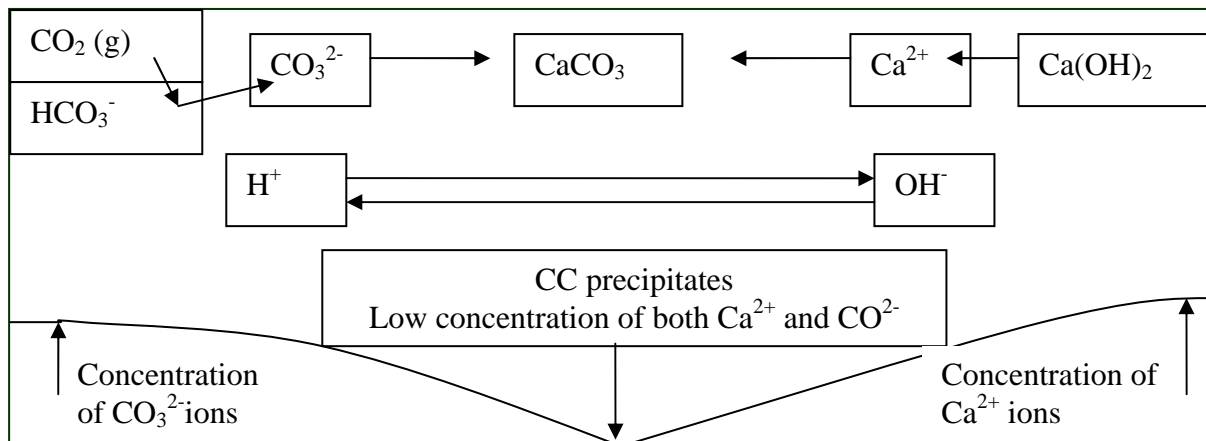


Figure 2. Schematic sketch of diffusion processes in a pore of a carbonating concrete. Where the CC precipitate depends on the concentration gradients.

To understand the different modes of carbonation and the effect on porosity between concrete made with plain OPC (CEM I) and with mixtures containing pozzolanas and GBFS we must identify the mode of precipitation. Moreover, we must consider the mechanism of the transformation and mode of nucleation of the carbonate. The carbonate may precipitate on the surface of the CH if the concentration of CO_3^{2-} is high but it may also precipitate in the pore solution or on other phases if the Ca^{2+} concentration is high. This will affect the porosity. Where the precipitation will occur will depend on the speed of diffusion of both Ca and carbonate ion to the point of calcite precipitation where the concentration of both components is low (see Fig. 3).

The most soluble phase is CH and it will thus be the first to dissolve and form carbonate. If carbonate ions move faster than Ca ions and the CC precipitates on the surface of the CH it will form a shell of CC around the CH that will hinder or slow down the carbonation. It seems, however, that the product is porous (Diamond 2000) and thus it will only delay it somewhat. If the Ca^{2+} move faster than the carbonate ions, the CH will dissolve and CC will precipitate as minute crystals in the capillary system. In this case, the volume change will result in a densification and decrease porosity. In paste with pure Portland cement this would lead to a shift towards a finer capillary system, which seems to be the typical case for pure Portland cement paste.

When the CH is consumed the carbonation will start to consume C-S-H. The C-S-H will dissolve in another mode than the CH. It is a cryptocrystalline compound with a backbone of short silica polymers bound together with Ca and OH ions. Leaching studies have shown that the C-S-H can lose substantial amounts of CaO without shrinking (Lagerblad 2001). When the paste is depleted from CH and the carbonation consumes Ca ions the C-S-H adjust by releasing CH. The equilibrium, which is linked to pH, will depend on the Ca/Si ratio (Stronach & Glasser 1997, Chen et al. 2004.) and the contents in the pore solution will drop successively. Thus the concentration gradient of Ca ions will drop and the diffusion will be slower. The concentration gradient of the CO_3^{2-} will, however, remain the same. Thus one can presume that the CC will precipitate close to the C-S-H and to a larger extent affect the gel porosity rather than the capillary porosity. This may explain why, for example, concrete made with slag cement gives another coarser pore system when carbonated (Stark & Ludvig 1997, Utgenannt 2004). This paste contains much less CH and more C-S-H. Moreover, especially

the concretes with GBFS and silica fume give more vaterite than calcite (Meland & Trätteberg 1981). Thus the coarser capillary pore system may be a consequence of the different mode of carbonation. A coarser capillary system in the carbonated shell will increase the speed of carbonation.

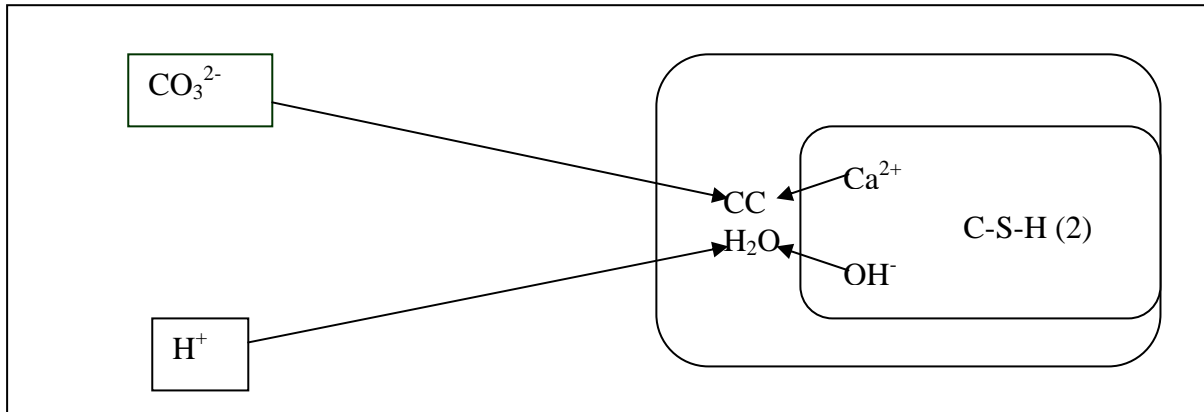


Figure 3. Sketch illustrating the mechanism when C-S-H becomes carbonated.

With slow diffusion of carbonate ions the C-S-H will consume all inward diffusion carbonate ions before it can react with CH further inside and therefore a rather distinct carbonation front will be obtained. Occasionally a double carbonation front can be observed where the CH carbonate in an inner front and the carbonation of the C-S-H form an outer front. This seems to be common in dry deserts where the carbonation is very rapid (Lagerblad 2003). This double carbonation front can also be observed in accelerated experiments with high contents of CO_2 in the air (Meland 1985). This is presumably due to that the release of CH from the C-S-H is too slow to consume all the carbonate ions. Thus some carbonate ions will pass only partly altered C-S-H and react with CH further inside. This phenomenon thus shows the difference in transport and reaction rate.

The cement pastes commonly also contain remaining unhydrated cement grains. These grains will probably slowly hydrate and subsequently carbonate late in the carbonated shell. Pozzolanas like silica fume or fly ash will change the proportions between CH and C-S-H. Likewise GBFS will give less CH and more C-S-H. Thus the carbonation process will rely more on C-S-H. As with the pure OPC the consequences will depend on the rate of diffusion, which in turn depends on the effect of carbonation on the porosity.

In conclusion; the carbonation process is chemically simple but in reality it is complex. It is a process where we have to consider that to propagate inwards the carbon dioxide and its ions have to pass its own alteration products. Thus we must understand not only the concrete quality and the environment but the mode of carbonation. This becomes especially important in understanding the carbonation of blended cement and the influence of mineral additives that is becoming more and more common.

3.2 Carbonation of wet or submerged concrete

Concrete submerged in water or wet concrete will also carbonate but much slower and in another mode. When the capillary system is blocked with water carbon dioxide gas has diffi-

cult to diffuse into the concrete. Thus for concrete submerged in water we have to consider the carbonate ions in water and not the CO₂ gas. Thus the rate of carbonation will be much slower (see above).

When the concentration of carbonate ions is low the carbonation rate will to a large extent be controlled by outwards diffusion of Ca ions and the carbonate will form at or close to the surface of the concrete (Lagerblad 2001, 2003). In the beginning, when the speed of diffusion of the Ca-ion is high, calcite will precipitate at the surface but when the speed of diffusion of the Ca ions goes down with time calcite will precipitate in the concrete causing it to become dense. The speed of leaching also depends on the circulation of water. Thus the rate of carbonation will to a large extent be controlled by the leaching process, which is very slow. In stagnant water the concentration gradient will diminish and the rate of leaching will decline. If the leaching rate of Ca ions is higher than the accessibility of bicarbonate ions the concentration of Ca ions and the pH of the water will increase. A normal concrete submerged in percolating water without erosion of the surface will leach less than 10 mm in 100 years and carbonates can only be observed in the outer 2-3 mm (Lagerblad 2001, 2003). Like carbonation, leaching approximately follows Fick's second law and the rate diminishes with the square root of time. One can, however, presume that all Ca-ions that leach will eventually form calcium carbonate either at the surface of the concrete or in the water. In soil the decay of organic matter may result in high CO₂ concentration but on the other hand the speed of the diffusion of CO₂ gas or carbonate ions in the soil may be slow.

In water bicarbonate is the stable carbonate ion. When the content of bicarbonate ions in the external water becomes low this will be compensated for by dissolution of carbon dioxide from the atmosphere. Thus also this reaction will bind carbon dioxide. A similar reaction will occur in wet concrete. If we assume that all the leached out Ca will be bound to carbonate this will be equivalent to a CO₂ uptake of carbonation to the same depth.

3.3 Carbonation of crushed concrete

Most concrete structures will eventually be demolished and the concrete crushed. This will result in much larger surfaces and expose fresh uncarbonated concrete to the environment. One must also consider that when crushed much of the cement paste will be a powder and much of it will form a skin on the larger stones. Thus the amount of exposed cement paste will be larger than what the crushing as such will give. This will increase the carbonation rate and CO₂ uptake considerably. Following the surface reactions the demolished concrete will follow the same rules as normal concrete and the rate will depend on the thickness of the cement paste and the rate will diminish with the square root of time. As the release rate of Ca²⁺ ions rate will be high one must also consider the accessibility of CO₂ and/or carbonate ions.

The rate of carbonation will then depend on the environment in which the crushed concrete will be placed. Due to the large reactive surface one can presume that surface reaction will carbonate a substantial amount of the cement paste of the concrete already before final end use. As a consequence one must consider local environment. As filling material or as a road base the humidity may be high and slow down carbonation. In this case the leaching may be faster than the carbonation process. The carbonation will then take place in the water when it accesses carbon dioxide.

4 Speed of carbonation

4.1 Fick's law and controlling factors

Concrete will carbonate whenever carbon dioxide and some water are available. The speed of carbonation depends on how fast the carbon dioxide and/or the carbonate ions can move into the concrete and react with the cement paste. In some cases, like in ground and submerged in water the accessibility of carbonate gas and ions may be the rate limiting factor. In the normal case, however, gas is available and we can assume a constant amount at the concrete surface.

Diffusion is mass transport down a concentration gradient. Steady state diffusion follows Fick's first law

$$J = D \frac{dc}{dx}$$

Where J is a quantity of a component passing through unit area per unit time, i.e. it is in this case the net transport rate of CO_2 and carbonate ions through a unit area and $\frac{dc}{dx}$ is the

concentration gradient/slope of molar concentration. D is a diffusion coefficient, a material property that depends on permeability, which in the case of concrete is the connective porosity. The carbonation process is, however, more complicated as it is a combination of gas and liquid transport, but it can still be simplified with Fick's laws.

Fick's second law gives depth of alteration/carbonation and not the amount of material that is being altered. In the non-steady state, where concentration changes in both space and time, we can apply Fick's second law where ∂t is a time factor. As before c is concentration and x is surface area.

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

It is difficult to solve this equation, especially as we have to take into account simultaneous inward diffusion of carbon dioxide, carbonate ions and outward diffusion of calcium ions. One must also consider solubility and precipitation as how this will affect the connective porosity. An effort to solve the coupled differential equations by using classic mass balance is presented in Bary & Sellin (2004). The complexity and the variability in factors necessitate simplifications. One such simplification that considers carbonation depth is presented in appendix 1.1.

The slow rate of carbonation in wet or humid environment shows that the speed of diffusion of the carbonate ions is comparatively low. Gas diffusion in a dry capillary system is rapid but the carbonation mechanism demands formation of carbonate ions, which in turn demands water. The diffusion coefficient D is a variable that depends on the microclimate, especially the RH inside the cement paste. Thus the calculation of CO_2 uptake must to a large extent rely on laboratory data, empirical data and measurements on real concrete structures. D values of the most important types of concrete must be estimated.

A detailed knowledge of all the parameters governing the rate of carbonation is impossible to gain. The carbonation gives moving boundaries and it can be simplified by coefficients that take the different ruling factors into account. Thus areas of major use must be identified and general assumptions regarding the speed of carbonation must be established. For each type of concrete given a specific environment the speed of carbonation can be calculated by

$$d_c = k\sqrt{t}$$

d_c = depth of carbonation

k = rate factor

t = time in years

With k -values for the most important types of concrete and environments it is possible to obtain a fairly good estimate of CO₂ uptake. This k value can then be corrected by a constant that considers cement types, cover, increasing partial pressure of CO₂ in the atmosphere etc. Subsequently it is possible to cover the whole range of carbonation situations.

4.1.1 Humidity

A very dry concrete does not carbonate due to the lack of water needed for ions to form and subsequently react and form calcite. On the other hand carbonation is also slow in wet conditions. This leads to a RH where the rate of carbonation is at maximum. This maximum will be at a specific RH, a specific open porosity and specific type of binder. Moreover, it also depends on the geometry of the capillary system, which in practice means that it depends on the water/binder ratio, degree of hydration and type of binder. The maximum speed of carbonation is when RH is somewhere between 60 and 80 % RH (inside the concrete). One would expect that a porous concrete will carbonate faster at a higher RH than less porous concrete as a narrow capillary more easily becomes blocked by water. This was also shown in accelerated experiments by Meland (1985). Cyclic wetting and drying seems to accelerate carbonation.

4.1.2 Temperature

The rate of diffusion and rate of the carbonation reaction increase with temperature. Thus indoor climate or exposure in warmer regions (Liang et al. 2000) will lead to faster carbonation if given all the other factors remain constant. This will mean a relatively low carbonation rate for outdoor concrete structures in the Nordic countries.

4.1.3 Binder content

The diffusion will occur in the paste and not through aggregate, assuming that the aggregate is dense. The amount of cement does not affect the rate of carbonation as long as the w/c ratio is kept constant (Concrete Society 1999). This is due to fact that the flux (J) is measured as material passing through a unit area and that the unit area becomes larger with an increasing amount of cement paste. Thus a larger amount of paste with the same porosity will give the same carbonation depth but a larger volume of carbonated paste. Thus, in order to estimate the carbonated paste volume, the amount of cement in the concrete mix must be known.

4.1.4 Concrete quality

Lower water/cement or water/binder and high degree of hydration give denser concrete with less connective porosity. It will also result in denser carbonate products and consequently

slow down carbonation in all environments. We can assume that a more dense concrete also gives a more dense carbonated concrete. This will affect the pessimum/maximum RH. With the same RH and finer porosity CO₂ gas will have more difficult to pass into the concrete and it will thus get a relatively lower RH pessimum for optimal carbonation. Thus the concrete quality will affect D . The pozzolanas will also affect the porosity and thus the speed of carbonation.

One must, however, also consider the degree of hydration. A lower degree of hydration will give a more porous paste. This will probably be the case in indoor environment with a low RH. In outdoor concrete structure surfaces, prolonged hydration will give rise to a densification of the intact paste that will give a more dense carbonated paste that with time will slow down carbonation. Thus the effect of bad curing will be important only in a short term perspective. It is also known that bad curing gives a higher rate of carbonation presumably due to the lower degree of hydration. The diffusion will be through the already carbonated layer and one must thus consider the effect when the remaining cement grains eventually carbonate. Remaining cement grains will probably react slowly with water and carbonate in the carbonated layer. This phenomenon has not been treated in any of the papers in the literature review. The effect of bad curing will probably diminish with time when the cement grains eventually hydrate and carbonate.

To be able to calculate the CO₂ uptake a general method must be applied. Considering the different types of cement/binder (see below) strength is probably the best. One can assume that there is a relationship between strength and porosity. Thus the strength will describe the porosity and can thus be used in the calculations. This applies for most concrete except some concrete products that have a coarse connective porosity.

4.1.5 Concrete structure/texture and cracks

The carbonation is a reaction from the surface and inwards. Thus the area of the exposed surface will be important. The diffusion will mainly occur in the porosity but one must also consider the interfacial zone between paste and aggregate and cracks. The interfacial zone is more porous and will thus give a faster carbonation. A deeper carbonation at the contact between paste and stones can commonly be observed in thin sections. In surface cracks (Liang et al 2000) carbon dioxide can reach deeper and will thus get a larger surface to react with. This can clearly be observed in thin sections where the walls of the cracks are carbonated. Thus the carbonation will also depend on durability and deterioration. A concrete affected by for example alkali silica or delayed ettringite reaction will crack and this will enhance the carbonation. Pieces of concrete that fall off will give new fresh surfaces and consequently higher rate of carbonation.

4.1.6 Partial pressure of CO₂

A higher amount of carbon dioxide in the atmosphere will increase the rate of carbonation (Fukushima 1988). Data are shown in appendix 1. The carbonation rate is higher in suburban areas and in the indoor environment where the partial pressure of CO₂ is higher. In some storage localities and industries the content of carbon dioxide may be very high. The lowest content is in coastal areas, as water will absorb carbon dioxide. Considering the global increase in CO₂ in the atmosphere the rate of carbonation will increase in the future. The effect of higher partial pressure on the carbonation rate is significant (see appendix 1.5). The k values suggested (chapter 5.1) are based on data from the past. In a calculation considering future CO₂ uptake the increasing contents must probably be considered.

4.1.7 Types of cement and effect of pozzolanas

In the Nordic countries pure Portland cement (CEM I) has been the most common type, but blended cements are becoming more and more common. These cements are mixtures of Portland cement clinker, gypsum, limestone, granulated blast furnace slag, fly ash, silica fume, volcanic ash, rice hush, burnt clay etc. They are all listed in EN 197. The type of addition/additive varies between countries due to tradition and availability of material. The most common type used for building purposes is CEM II. This cement is becoming more and more common due to the relatively lower environmental impact to the society. Commonly CEM II contains more than 80 wt-% Portland cement clinker but sometimes it contains more.

Apart from being a part of and being delivered as part of the cement, the additives can be added during concrete mixing. Fly ash and silica fume are often added separately. The speed of carbonation is often related to the water/cement or water/ binder. Due to the different types and different reactivity w/c and w/b is difficult to use. Thus the carbonation rate has to be related to strength (see 4.1.4) to give an accurate value. As some of the reactions are slow the normal 28 days strength is probably not accurate but this is in most cases the only value known and must thus be used. A small correction value should, however, be given since many of the blended cements have a higher late strength than pure Portland cement.

The additives can be divided into three groups, inert mineral fillers, latent hydraulic binders and pozzolanas.

Portland-limestone cement (CEM II/L and CEM II/LL) consists of Portland clinker that has been ground together with limestone. A result of the co-grinding is that the cement contains ultrafine calcite particles. Normally the mixed cements in the Nordic countries (CEM II A-L) contain between 10 and 20 wt-% replacement and they give the same strength and have the same strength development as normal CEM I, i.e. the ultrafine limestone has a strength efficiency factor of 1. All ultrafine particles give the same result and the effect seems to come from particle packing and from the fact that the ultrafine particles become an integrated part of the cement paste (Lagerblad & Vogt 2004). The proportion between the different hydrate phases is the same as in pure Portland (CEM I) cement. We can assume that the porosity is the same for the same water/binder ratio and strength. If this is the case the Portland-limestone cement concrete will carbonate somewhat faster (in depth) as the amount of Portland clinker cement paste and the buffering capacity is less. If we assume the same porosity and environmental factors the increase speed of carbonation will be linked to the amount of filler. The degree of hydration will, however, be somewhat higher thus the effect will be less. With 10-20 % replacement we can presumably calculate with a 5-10 % higher rate of carbonation. Better empirical data are, however, needed.

Portland-slag cement (CEM II/A-S) contains up to 20 % blast granulated furnace slag (GBFS). CEM II/BS contains up to 35 % and CEM III contains between 35 and 95 % GBFS. Granulated blast furnace slag is a latent hydraulic binder, i.e. it will be a binder by itself if activated, commonly by Portland cement. Thus one can find mixtures in all proportions. The slag cement paste contains less CH and more C-S-H. Moreover the C-S-H will contain more Al and Mg. Thus the carbonation process and the structure of the carbonated paste will be different. Most evidence shows that combinations of Portland cement and GBFS carbonate faster (Meland & Trätteberg 1981, Parrot 1986). This is probably due to the fact that the structure of the carbonated concrete has a coarser pore structure that will enhance speed of diffusion (see chapter 3.1). According to Häkkinen 1993, however, concrete with slag in the binder carbonate faster in the beginning but the rate is similar to pure OPC in old concrete.

Presumably one has to calculate with a somewhat higher rate of carbonation (in depth) than from pure Portland cement. The carbonation rate seems to increase with the amount of GBFS. When based on concrete strength we can probably assume a similar increase of carbonation rate as with limestone filler, i.e. the increase will be about half of the amount of GBFS.

Fly ash and volcanic ash are both a filler and pozzolana. Silica fume is a highly reactive pozzolana. Pozzolanas exist in several modifications. They are either added at the cement factory (CEM II D, P, V and T) or mixed with the Portland cement at the concrete factory. In some countries the amount of pozzolana is so high that it is the major component of the cement (CEM III and CEM IV). All the pozzolanas react pozzolanically but to a different degree and at a different rate. In the pozzolanic reaction CH will be consumed and the amount of C-S-H will increase. The most common types of pozzolana in the Nordic countries are fly ash and silica fume. They will both change the mode of carbonation and the structure of the carbonated layer like the GBFS (chapter 3.1). The effect will depend on the type of and amount of pozzolana. Silica fume is the most efficient pozzolana and reacts already in the early hydration process while fly ash will react with already formed CH. Less CH will increase the rate of carbonation (in depth) but one must also consider the increased amount of C-S-H and the effect of this on the already carbonated paste. Moreover, especially in the case of silica fume, the porosity is finer. In the case of fly ash, only parts of it react pozzolanically and thus part of the effect is due to the filler effect (see above). Thus the reactivity of fly ash must be considered for the specific type.

In concretes with and without silica fume those, concrete with silica fume seem to carbonate somewhat faster. This is shown from natural carbonated concrete structures by Maage & Skjölsvold (1983). With other pozzolana it is difficult to find a good comparison. Fly ash has different reactivities and fineness and this gives different results. In a series of experiments Meland (1985) concluded that fly ash blended cements do not carbonate faster than CEM I cement. These, like other experiments, were conducted on relatively young concretes and in accelerated tests with high partial pressure of CO₂. In the young concretes blended cement may give higher porosity as they harden slower, and higher CO₂ contents in the tests will give another mode of carbonation. It seems, however, that with a given strength the concrete with pozzolana carbonates faster (Meyer et al 1967, Ali & Dunster 1998). If we assume that mixes with pozzolanas gives the same strength and connective porosity as concrete with pure Portland clinker, the amount of calcium to be carbonated will be less and thus the carbonate ion can penetrate to a larger depth. The carbonation rate increases with the amount of fly ash (Nagataki et al. 1986). Comparisons between concrete with and without fly ash (Matthews 1984) show that with the same strength class fly ash concrete carbonates somewhat faster. Silica fume reduces the amount of CH but makes the concrete denser. These will, however, affect the strength of the concrete, and if we calculate the carbonation rate on the basis of strength, the carbonation rate must increase. With silica fume in the range 5-10 % we can probably expect an increase in carbonation rate. To obtain a good value for fly ash we must know the amount of fly ash used and the effect of this fly ash on concrete in terms of strength. If we correlate porosity and strength and calculate carbonation rate on strength, the rate of carbonation (in depth) will probably increase somewhat with strength. We can assume/estimate that the carbonation rate in each strength class increases with around half of the amount fly ash added.

4.1.8 Other

The speed of carbonation depends on the rate of diffusion of CO₂ through a surface. Thus paintings or wall paper etc will decrease the rate of carbonation. Silanol, silane, siloxane and

other types of surface treatments intended to protect concrete will give less RH in the pore system and will thus speed up the carbonation in outdoor structures. Porous cement bound materials will carbonate fast as the surface area between cement paste and air will be large. Thus the strength relationships do not apply to porous concrete. Air can penetrate the blocks, the reactive surface will be larger and consequently the rate of carbonation will thus be fast.

Some structure suffers from frost damage. As flakes of concrete fall off, new surfaces will appear and the rate of carbonation will increase.

4.2 Examples of uses, concrete details and environments

4.2.1 Use of concrete

To be able to calculate CO₂ uptake we must know where the concrete is used and the surface of the objects in which the concrete is used. These aspects can be divided into areas of use, concrete costumers and concrete products etc. How the material is to be divided depends on available statistics.

Two major consumers are readymixed and precast concrete. As regard carbonation, however, the most important is the use and the end-use after demolition. We can assume that all houses in the Nordic countries are subject to similar environments. Thus independently of whether houses are cast in-situ or prefabricated, adjustments must be made for factors such as strength, type of cement etc.

How the material is sorted depends on available statistics. One such sorting may be areas of use.

- Houses
- Bridges
- Dams
- Harbour constructions
- Road bases
- Concrete road and pavements
- Concrete products

Most of these areas are broad. Thus to obtain an accurate basis for analysis the material from each group has to be subdivided into structural elements. The environment and surface area of the individual structural details have to be analysed then put together again in areas of use.

Typical structural elements:

- Wall elements
- Columns
- Beams
- Bridge details
- Pavement slabs
- Concrete blocks
- In situ cast slabs
- Hollow core slabs

- Paving stones
- Pipes
- Bricks
- Tiles

After ended use the concrete structures will be demolished. The applications and the environments of these applications have to be identified.

4.2.2 Environments

Carbonation is the result of diffusion of CO_2 and carbonate ions from the environment into the concrete where it reacts with the cement paste and form CaCO_3 .

The relevant environments we can identify are

- Indoor concrete
- Outdoor sheltered
- Outdoor exposed
- In underground (rocks or soil)
- Submerged in water
- Industrial environments
- Farming structures

For each of these environments we assume standard Nordic conditions as regard RH, temperature, partial pressure of CO_2 etc. The data used must thus come from Nordic or northern hemisphere conditions. Some deviations must, however, be considered and taken into account.

Particularly with respect to the first three environments one must also consider that if the surfaces are painted or covered this will slow down the carbonation. For indoor concrete one must also consider the effect of wall paper. This has to be considered and thus the rate of carbonation will be lower than for exposed concrete surfaces.

In indoor environments, one can presume that the temperature and RH are fairly constant over the year. In some industries, the indoor climate can, however, be very dry or wet, which both slow down the speed of carbonation. The RH is also higher in some wet areas like in the bathroom. To be able to calculate the CO_2 uptake an average value must be given. Minor areas of applications have to be neglected or a correction factor must be established.

In outdoor climate, the first subdivision is between sheltered and exposed conditions where the exposed conditions are wetter and thus carbonation is slower. One must, however, also subdivide between vertical and horizontal surfaces as vertical surfaces dry much faster than horizontal ones and thus carbonate faster. Driving rain will also make the vertical concrete surfaces wetter and will thus decrease the rate of carbonation. An average value must be estimated based on statistics.

Some details of outdoor infrastructure concrete will also be covered like the roads on bridges and the concrete will thus carbonate very slowly.

Underground concrete has less access to atmospheric CO₂ but in bases and concrete for soil stabilisation etc one must consider biological decay that produces new CO₂. This means that diffusion of CO₂ in the soil will be important. There are many types of soil and cover but one can assume that in all of them the diffusion rate and thus the rate of carbonation will be low. This must, however, be verified.

5 Calculation of CO₂ uptake

All concrete and other cementitious materials will carbonate when in contact with carbon dioxide and carbonate ions. As carbon dioxide and carbonate ions can be found in almost all environments on earth it is a matter of time before all concrete is carbonated and the calcite from the limestone calcinated during cement production is back to calcite. Thus the CO₂ uptake must be considered in a time frame. The CO₂ uptake can be calculated as follows:

1. How much CO₂ has up to now been taken up from when cement was invented
2. How much CO₂, within a defined time, is being taken up today
3. How much CO₂, within a defined time, will be taken up in the future by concrete produced today
4. How much CO₂, within a defined time, will be taken up in the future by concrete produced in the future

As the CO₂ uptake is time dependent we must know the relevant data of the concrete produced in the past and concrete being produced today and relate this to the speed of carbonation. If we want to know the future CO₂ uptake we must also estimate concrete production and types of cement used in the future.

A detailed knowledge of all of the parameters governing the rate of carbonation is impossible to gain. Thus areas of major use must be identified and general assumptions regarding speed of carbonation must be established. To estimate the speed of carbonation we must rely on rate factors and calculate the depth of carbonation over time. This is simplest done by the following equation, which is based on simplifications of Fick's second law (chapter 4.1).

$$d_c = k\sqrt{t}$$

d_c = depth of carbonation

k = rate factor

t = time in years

The different k values must be identified for different concretes and environments. When surfaces, depth (d_c) and the amount of cement in the concrete are identified the CO₂ uptake can be calculated.

The types of structures and products consuming most cement must be identified. The general types of cement and the concrete qualities used in these structures and products must be identified. Moreover, the environments in which these structures are located by must be identified. This is discussed in chapter 4.

The rate of carbonation is linked to porosity, which in turn can be related to either the strength or water/binder. This relationship is, however, becoming less clear due to the increasing use of blended cements and different cement additions. The most simple is to use strength as this is linked to porosity and porosity is one of the most important factors as regard carbonation. In the literature carbonation is often linked to w/c or w/b but for this purposes the k -value has to be linked to strength.

Different types of applications normally have specific quality requirements and types of cement. For each major application we must know the exposed surfaces and the local environment that these surfaces are exposed to. With some assumptions the CO₂ uptake for each category can be calculated.

In all environments the rate of carbonation decreases with time, i.e. the rate of CO₂ uptake will be small for an old structure. Eventually, however, most of the concrete structures will be demolished. Most concrete, except some thin products or structural units, will not be fully carbonated before demolition. When the concrete is demolished it will expose new surfaces with fresh paste and a new cycle of CO₂ uptake will start. This means that for long time scales we have to make a distinction between structure life time, demolition and end use of demolished concrete.

If we know the amount of carbonated concrete, the amount of cement in this concrete, the amount of CaO in the cement and proportion of this CaO that has carbonated it is possible to calculate the amount of Portland cement clinker that has regained its CO₂.

5.1 Numerical calculation of CO₂ uptake

Carbonation of concrete is a surface phenomenon, i.e. the CO₂ uptake is related to the exposed surface. The available statistics are either in m³ of concrete or in tons of cement consumed in a specific quality of concrete. Thus the cement used for a specific structure or cementitious product has to be recalculated to exposed surface.

As a first step, the most important types of concrete structures and environment must be identified. As the porosity of the carbonated concrete is difficult to find one must make some assumptions.

5.1.1 Strength classes

The porosity of the carbonated concrete is related to the strength of the uncarbonated concrete. With four strength classes most of the concrete can be covered.

<15 MPa (Old concrete and some concrete products like cement bound blocks)

15-20 MPa (Old houses and some products)

25-35 MPa (Most houses today)

> 35 MPa (Most infrastructure concrete)

5.1.2 Environmental classes

The effect on the k -values has to be estimated from general types of environment. All concretes are assumed to be subjected to typical Nordic climate and empirical data from this. For in-

doors climate winter heating is assumed. The k -values below are estimated from data in appendix 1, values from other articles and consultancy reports from CBI. This is a first estimation and the values may have to be corrected when more data appear.

Table 2. Suggested k -values for concrete surfaces with CEM I and exposed concrete surfaces. Strength class in cylinder strength values (C). Buried concrete is concrete in the ground not in direct contact with the atmosphere.

Strength	< 15 MPa	15-20 MPa	25-35 MPa	> 35 MPa
Wet/submerged	2 mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0,75 mm/ $\sqrt{\text{year}}$	0,5 mm/ $\sqrt{\text{year}}$
Buried	3 mm/ $\sqrt{\text{year}}$	1.5mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0.75mm/ $\sqrt{\text{year}}$
Exposed	5 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$	1.5 mm/ $\sqrt{\text{year}}$	1 mm/ $\sqrt{\text{year}}$
Sheltered	10 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	4 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$
Indoors	15 mm/ $\sqrt{\text{year}}$	9 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	3.5 mm/ $\sqrt{\text{year}}$

The k -values in Table 2 are based on generalisations considered when the k -values are estimated.

Indoor concrete is exposed to higher temperatures than outdoor concrete in the Nordic countries. Higher temperature gives a higher rate of carbonation. The values mostly come from empirical data and are thus taken into account in the k -values. Industrial buildings may have different environmental factors. The amounts of concrete for these applications are probably minor and can thus probably be neglected. Likewise an increase in CO₂ content in the atmosphere is neglected. This may have to be considered in calculations in a hundred years perspective from now. According to data from Fukushima (1988), an increase from 0.03 to 0.06 % CO₂ in the atmosphere will increase the rate of carbonation 5 times. Thus a factor should at least be considered. It is suggested that in the calculation for 50 or 100 years from now a factor of 1.5 should be put on the k -value of all concretes.

The k -value of “Buried” concrete depends on biological decay and density of the soil/ground. Although the partial pressure of CO₂ often is high due to biological decay the diffusion is slow and the rate of carbonation will consequently be low. Thus a value of slightly more than wet/submerged concrete is assumed but the variation may be large. For bulk volume concrete like for demolished concrete a more specific value may be needed.

For wet/submerged concrete a water percolation is assumed. With stagnant water the rate of carbonation will be lower.

5.1.3 Correction factors for surface treatment and cover

The k -values for the concretes are for exposed “naked” concrete. Very often the surface is covered by carpets, paints etc. This is probably the reason why the depth of carbonation from the CBI record (Fig. 1 in appendix 1) is lower than expected. From some consultancy reports where concrete strength and age are known it seems like surface cover like paint is lowering the rate of carbonation by 30-50 %. The exact rate depends on the type and thickness of surface cover. We can assume that wallpaper will slow down carbonation in a similar way. Thus the k -value for indoor concrete has to be lowered. As a first rough estimate we can assume that it will be lowered by around 30 % compared to naked concrete. Assuming this, the k -value for a normal indoor concrete will be 4.5 instead of $6 \text{ mm}/\sqrt{\text{year}}$. Likewise, some outdoor surfaces, especially on buildings are painted and the rate of carbonation must be adjusted. The amount of painted surfaces is less and the paint is different. On the other hand painting repels some of the water, makes the concrete drier and thus gives a higher rate of carbonation. It is suggested that at least for the facades and balconies of houses the k -value should be reduced by 10 %. Infrastructure concrete is today often covered by a layer of wax to protect from graffiti. This will slow down carbonation. On the other hand some surfaces are treated with silane/siloxane which will dry out the concrete and thus increase the rate of carbonation. Presumably, the overall rate of carbonation for infrastructure concrete is close to that of the naked concrete.

Table 3. Correction factors for surface treatment and cover.

1	Indoor house concrete	$k \times 0.7$
2	Outdoor house concrete	$k \times 0.9$
3	Infrastructure concrete if painted	$k \times 1.0$

Indoor concrete is normally covered with some materials and thus the correction factor must probably be used. A factor of 0.7 is thus suggested. Outdoor house concrete is often covered by some kind of paint or other type of material and thus a lower value than that in Table 2 must be used. A factor of 0.9 is thus suggested. Infrastructure concrete like bridges etc is mostly uncovered and surface treatments are becoming common. This probably balances out and thus no correction factor is suggested.

5.1.4 Correction factors for type of binder

The carbonation rate values above have been derived from CEM I. Today additions/additives are becoming increasingly more common. The effect on the carbonation rate is discussed chapter 4.1.7.

Today, CEM II with inter ground limestone is largely used for residential buildings. In Sweden the 15 % of the cement clinker in CEM II (byggcement) is replaced with co-ground limestone. The cement gives the same strength as a CEM I. If we assume that concretes with the same strength have a similar porosity in the carbonated layer the only difference would be the amount of hydrated cement grains. The proportion between the different hydrates will be the same. A lower amount of cement will reduce the buffer capacity. Thus the speed of carbonation (in depth) will be higher. With the assumptions above and 15 % replacement the rate of carbonation would be 15 % higher. One can, however, expect a higher degree of hydration

and thus this value would be somewhat lower. Thus a 10 % higher k -value seems reasonable. Thus with CEM II and 15 % replacement the k -values above should be corrected with a 10 % higher value. With higher contents of limestone replacement the k -value will increase accordingly.

Silica fume gives a somewhat stronger concrete but carbonate at a similar or somewhat faster rate (see chapter 4.1.7). Thus using strength classes a factor above 1 must be used. With the same strength the rate of carbonation with 5 to 10 % silica fume the rate of carbonation probably goes up around 5 %.

Fly ash will give a stronger concrete with less cement. It is commonly used in Denmark. It is either co-ground with the cement or added at the concrete plant. With pozzolanic fly ash, however, the proportion between the different cement hydrates will change. The cement paste will contain more C-S-H and less CH., which in turn will affect the carbonation rate. Fly ash if fine will also give a filler effect like in the lime stone cements. The fly ash probably has higher effect on strength when co-ground due to finer grain size. The combined effect is difficult to calculate but from empirical data with the same strength the rate of carbonation (in depth) will increase. The effect of fly ash will depend on the amount and type used. We can probably with moderate amounts make a similar estimate as with the limestone, and give it a binder factor of above 1.

The slag cement probably gives a somewhat higher correction factor than fly ash.

The values below are conservative approximations and may have to be corrected when more data is available.

Table 4. Binder correction factors based on strength classes. % in weight of binder.

Amount in wt. %	<10	10-20	20-30	30-40	40-60	60-80
Limestone		$k \times 1.05$	$k \times 1.10$			
Silica fume	$k \times 1.05$	$k \times 1.10$				
Fly ash		$k \times 1.05$		$k \times 1.10$		
GBFS	1.05	$k \times 1.10$	$k \times 1.15$	$k \times 1.20$	$k \times 1.25$	$k \times 1.30$

5.1.5 Calculation of CO₂ uptake

The calculations will give the depth of carbonated concrete at a given time. From the concrete mix the amount of carbonated paste and cement can be calculated. In a carbonated concrete as defined by phenolphthalein, 75 wt % of the CaO in the Portland clinker will be consumed by the carbonation (chapter 2). Once given the amount of cement paste/cement, the CO₂ uptake can be calculated.

$$\text{CO}_2 \text{ uptake} = a = 0.75 \times C \times \text{CaO} \times \frac{M_{\text{CO}_2}}{M_{\text{CaO}}} \text{ (kg / m}^3\text{)}$$

0.75 amount of CaO carbonated (Chapter 2)

C = Amount of Portland cement in concrete per m^3

CaO = amount of CaO in cement (wt-%).

M = molar weight of oxide

This calculation will give the CO_2 uptake.

5.2 Example; Calculation of the CO_2 uptake of a house

Houses/buildings consume most cement/concrete and most of the concrete is of a similar quality. In each Nordic county one type of cement or binder combination is normally used for houses. Today in Sweden almost all concrete buildings are made with “Byggcement”, which is a CEM II with limestone filler. Earlier a CEM I cement was used. The concrete quality is normally around C25-C30. For this strength quality around 300 kg cement per m^3 of concrete is used. We can also assume a Nordic outdoor climate and a normal indoor climate at around 20-25 °C. Indoor climate is assumed to be dry while outdoor climate is either wet or semi-dry sheltered. There are climatic variations over the year but an average speed of carbonation from existing structures in Nordic climate has to be used. (See below)

Given this and the amount of cement used for house construction we need exposure areas divided into different environments. The local microenvironment for each detail will be impossible to calculate but it can be divided in general groups with a similar environment. The division below is a suggestion and other ways of subdividing the material is possible. Some areas of use may be too small and can be neglected.

A similar division and calculation have to be performed on all types of concrete.

Example for 1 m^3 of concrete used for buildings

1. Ground foundation; a % gives a surface of $a_1 \text{ m}^2$.
2. Floors structures; b % gives a surface of $b_1 \text{ m}^2$. Top of ground foundation is also a floor.
3. Walls indoor; c % gives a surface of $c_1 \text{ m}^2$
4. Staircases; d % gives a surface of $d_1 \text{ m}^2$.
5. Walls outdoor; e % gives a surface of $e_1 \text{ m}^2$.
6. Balconies; f % gives a surface of $f_1 \text{ m}^2$
7. Other; g % gives a surface of $g_1 \text{ m}^2$

$a + b + c + d + e + f + g = 1 \text{ m}^3$ concrete.

To be able to do this an average value of how thick the different details are must be estimated.

Carbonation is a surface phenomenon. Thus the amount of concrete must be recalculated to exposed surface for the specific details.

$$a_1 + b_1 + c_1 + d_1 + e_1 + f_1 + g_1 = x \text{ m}^2 \text{ exposure surface}$$

The different surfaces must be linked to a specific environment, exposure class.

There are four main exposure classes for a concrete house. The carbonation rates (k -value) comes from chapter 5.1. It is assumed that CEM II/L cement (byggcement with 15 % limestone gives a correction factor of around 1.05) is used, the concrete strength is around 30 MPa and correction is made for cover. Basic κ -values from Table 2, surface protection values from Table 3 and binder correction values from Table 4

- | | |
|--|---|
| 1. Indoor (fast carbonation) | k -value $\approx 6 \times 0.7 \times 1.05 \text{ mm}/\sqrt{\text{yr}}$ |
| 2. Outdoor sheltered (medium fast carbonation) | k -value $\approx 4 \times 0.9 \times 1.05 \text{ mm}/\sqrt{\text{yr}}$ |
| 3. Outdoor exposed (slow carbonation) | k -value $\approx 1.5 \times 0.9 \times 1.05 \text{ mm}/\sqrt{\text{yr}}$ |
| 4. In ground (slow carbonation) | k -value $\approx 1.05 \times 1.0 \times 1.0 \text{ mm}/\sqrt{\text{yr}}$ |

If we look at the different concrete details a subdivision may be

- | | |
|---------------------------|--------------------------------------|
| 1. Ground foundation | 50 % in ground and 50 % indoor floor |
| 2. Floor | 100 % indoors |
| 3. Walls indoor | 100 % indoors |
| 4. Staircases | 80 % indoor 20 % sheltered |
| 5. Walls outdoors. | 50 % is exposed and 50 % indoor |
| 6. Balconies. | 50 % sheltered 50 % exposed |
| 7. Others, roof tiles etc | 50 % exposed 50 % sheltered |

From area and exposure class and time we can calculate the volume of concrete carbonated.

The amount of concrete carbonated $\text{CaO} = (k_1 a_1 + k_2 b_1 + k_3 c_1 + k_4 d_1 + k_5 e_1 + k_6 f_1 + k_7 g_1) \sqrt{t}$. The amount of CaO will consume an equivalent molar amount of CO_2 . Some of the concrete details are exposed to different environment. Thus an average k_i value based on the % exposure class of each detail must be estimated. It can also be divided in % exposure surface but the result will be the same.

The calculation will give the amount of carbonated concrete at a given time. From the concrete mix, the amount of carbonated paste and cement can be calculated. In a carbonated concrete as defined by phenolphthalein 75 wt % of the CaO in the Portland clinker will be consumed by the carbonation (chapter 2). Thus given the amount of cement paste/cement, the CO₂ uptake can be calculated according to the formula in chapter 5.1.5

This calculation will give that with an age of 50 to 100 years between 32 and 60 mm will be carbonated in indoor climate with a k -value of 4.6. However, even with a higher carbonation rate a substantial amount of uncarbonated concrete will remain.

If we also consider that some details will carbonate slower and that most concrete buildings will not last more than 100 years a substantial amount of uncarbonated concrete will demolished and much of the carbonation will occur after demolition.

Similar types of calculation can be made from the other types of concrete structures and products. We mainly need area of exposed surfaces, k -values adjusted for microclimates and time.

5.3 Examples; Calculation of CO₂ uptake for details.

5.3.1 Element exposures

To do this type of calculation we must first identify the different details of the elements, the type of concrete used in them, the concrete surface and the exposure environment for the considered structural detail.

Type of detail	Exposure	Exposure comments
Pavements	Exposed/buried	Half is buried and half exposed to outdoor climate.
Blocks	Exposed/buried/indoor	Depends on use of blocks. Walls of blocks can be treated like façade elements.
Elements	Indoor	Elements will be paint covered.
Façade elements	Outdoor/indoor	Half of the façades will be indoors. The outdoor ones will be sheltered
Slabs, hollow core	Indoor	The holes will also be indoors. Surfaces covered or painted.
Slabs, massive	Indoor	Surfaces covered or painted
Slabs on ground	Indoor/buried	Half in ground half will be floor with cover
Pipes	Buried	Can be carbonated on the inside, depends on use.
Tiles	Outdoor	Half is exposed and half is sheltered
Columns/beam	Outdoor/indoor	Part of the outdoor ones like in garages will be sheltered.
Bridges	Outdoor	Half exposed and half sheltered.
Marine structures	Outdoor/wet	Most of the surfaces are in exposed outdoor environment
Dams	Outdoor/wet	Massive structures with small surfaces

When the data above are identified, the carbonation rate of the considered element detail, for a certain time period, can be calculated. This, however, demands that we know average values of surface, surface environment, strength class, type of binder etc.

In-situ cast and precasted concrete will be the same and if there is a difference this will be adjusted for strength class and binder type. Likewise, the type of concrete pavements must be identified. Whether they are concrete roads or concrete block pavements must be specified. For the infrastructure concrete the amount used in bridges, harbours, etc must be identified. The material must first be split up into different types of concrete elements and details and then put together again to get an average value for the different major areas of use. Following this it has to be split up into types of cement, strength class etc for the different years in the past and an evaluation of what might happen in the future. How this is done depends on what type of statistics are available.

5.3.2 Examples of CO₂ uptake for different elements are given below

Hollow core slab

- Slabs Hollow core. Made today
- Thickness 300 mm
- Surface/m³ concrete = Outer surface = 6.6 m² inner surface 3 m² (the holes)
- Environment Indoor
- Strength class C30
- Environment Indoor
- Cement CEM II/L 360 kg (15 % L)
- Amount of pure Portland cement 306 kg

A C30 indoor concrete has a k -value of 6 mm $\sqrt{\text{year}}$. The holes have naked concrete, while the upper surface probably is covered by some type of floor cover. The lower side (roof) is probably painted. The floor cover lowers the k -value significantly and the paint somewhat. On an average we can assume a decrease in the k -value of 30 %, i.e. k -value will be 4.2 instead of 6. The CEM II/L carbonates somewhat faster and must be given a correction factor of around 1.1. i.e. the k -value will be 4.6. With this k -value the concrete will carbonate to a depth of 32 mm in 50 years. With an exposure area of 9.6 m² 0.31 m³ of the original m³ concrete will have carbonated. This concrete contains 95 kg of pure Portland cement. A normal pure Portland cement contains around 65 wt% CaO. If we assume that 75 % of the CaO in the cement has carbonated 46 kg of the CaO has been converted to CaCO₃ (see Chapter 5.1.5). From this the amount of CO₂ uptake can be calculated.

Cast in situ floor

- Floor Massive concrete
- Environment Indoor
- Thickness 150 mm
- Surface/m³ concrete 13.2 m²
- Environment indoor
- Strength class C30
- Binder amount 350 kg/m³
- Binder type CEM II/L (15 % L)
- Amount of Portland cement 298

A massive floor is similar to a hollow core slab, but we do not have to consider the holes. A C30 indoor concrete have a k -value of $6 \text{ mm} \sqrt{\text{year}}$. Most of the walls will be covered either by wall paper or paint. On an average we can assume a decrease in the k -value of 30 %, i.e. the real k -value will be 4.2. This value is based on CEM I and CEM II/L will give around 10 % higher k -value, i.e. 4.6. In 50 years around 32 mm will be carbonated. This will be equivalent to 0.43 m^3 concrete. The carbonated concrete contained 150 kg CEM II/L which is equivalent to 128 kg CEM I (15 % limestone). This concrete contains around 83 kg CaO (65 % of clinker). From this the CO_2 uptake can be calculated.

Facade elements

• Facade elements	Massive concrete cast today
• Environment	Half outdoor/half indoor
• Thickness	200 mm
• Surface/ m^3 concrete	10 m^2
• Strength class	C30
• Binder amount	350 kg
• Binder type	CEM II/L (15 % L)
• Amount of Portland cement	298 kg

A C30 indoor concrete has a k -value of 6 mm that with a paint/wall paper correction and CEM II/L correction gives around $4.6 \text{ mm} \sqrt{\text{year}}$. A C30 outdoor concrete will have a k -value of between 1.5 and 4 $\text{mm} \sqrt{\text{year}}$ depending on the degree of shelter. We can assume an average value of 2.5 mm. This has to be corrected for the possibility of painting. We can assume a reduction of 10 % due to painting. This would give a k -value of $2.25 \text{ mm} \sqrt{\text{year}}$. With corrections for CEM II/L this gives a k -value of $2.47 \text{ mm} \sqrt{\text{year}}$. This means that during 50 years 5 m^2 of concrete will have carbonated to a depth of 17 mm while 5 m^2 will have carbonated to a depth of 32 mm. In total 24.5 % of the concrete will have carbonated. This will result in 47 kg of carbonated CaO.

Data from this type of calculation must be put together to groups given by the statistical material available.

6 Discussion

With enough time all concrete structures will carbonate. The CaO of the blast furnace slag and fly ash will also carbonate. With knowledge of types of concrete produced over time and the types of structures this concrete was used in it is possible to make a calculation but the carbonation and CO₂ uptake must be put in a time perspective. To be able to calculate the CO₂ uptake we must make some assumptions. Demolition is one of the most important.

- 1 Concrete structures will be demolished after a service life of between 50 and 100 years. Houses on an average will last for more than 50 years and infrastructure concrete more than 75 years. In the future, the life-time of infrastructure concrete in particular will presumably be longer. An average age of 75 years for houses and 100 years for most infrastructure elements is suggested.

Fifty to one hundred years after construction the carbonation process will be very slow as the speed of carbonation diminishes with the square root of time. Additional uptake from undamaged surfaces after 50-100 years can almost be neglected.

- 2 After being demolished the concrete will be crushed and the crushed concrete will be subjected to atmospheric conditions. After demolition and crushing most of the concrete will, if subjected to air, probably carbonate within 10 years.

This will result in most of the cement paste becoming be carbonated in 100-150 years.

If we want to find out the CO₂ uptake tomorrow and in the future we must consider both older structures as well as structures built today. For the buildings built today we have good data from production and requirement. For older structures we must examine records to find out about areas of use and type of cement. In the future we can expect a higher rate of carbonation due to the global increase in partial pressure of CO₂.

The carbonation rate depends on the environment. It will be impossible to find the precise microenvironment for each concrete surface. Thus the surfaces have to be divided in broad groups. Indoor, outdoor sheltered, outdoor, underground and wet submerged are probably the most common types of environment/surfaces and data for these types must be established. The way the material is classified and the analyses performed will depend on the available statistics.

7 Conclusions and work to be done

It is possible to calculate the amount of CO₂-uptake but considerable knowledge is required.

1. Time frame for calculation
2. Use of concrete over time
3. End uses of concrete in different types of structures and cement based products
4. Amount of concrete/cement used in the different end uses.
5. Surface area of the different products and structure details related to amount of concrete/cement.
6. Exposure environments for the different surfaces
7. Speed of carbonation (k -value) for different concrete qualities, concrete with different types of cement and in different environments. The values suggested must be adjusted when more data are available.

If data for all of these parameters are available an accurate analysis of depth of carbonation can be calculated and put into a time frame. It will, however, be impossible to obtain accurate statistics and data that cover all types of concrete constructions and concrete materials. Simplifications and assumptions must be made. Firstly, however, the time frame for calculations must be decided.

Basic assumptions for calculation;

1. The CO₂ uptake today from older concrete structures
2. The CO₂ uptake from one year of cement production in a 20, 50, 100 and 150 years perspective

Major cement/concrete areas of consumption

1. Houses
2. Infrastructure
3. Pavements
4. Others

The types above will include x % of the cement consumption. Since all concrete elements and products can not be covered, the most important areas must be identified and the calculations must be based on the areas with a general estimate regarding the other products. From statistics we must find how much of the cement/concrete that goes to the different applications and based on the available statistics the material must be grouped. The available data will probably be in broad groups not aimed for this type of calculation. Thus the material must be split up into relevant categories and then compiled into groups in order to obtain statistics. This

means that we have to go into specific structure elements and details and make assumptions based on them.

We have to assume a specific concrete quality for the different applications. For the past we can assume a similar or lower quality. For long term calculations we probably also have to take future increases in CO₂ content in air into account.

The data on carbonation rates are either related to water/binder ratio or strength. Strength data are the most convenient to use. Using strength data we do not have to consider different types of pure Portland cement, but we must make correction factors for different types of blended binders. Moreover, the available data on carbonation rates comes from “naked” concrete. Correction factors must be given for different types of surface treatments and cover. The data available for surface treatments and cover are inadequate. Therefore a study needs to be conducted in this area.

The calculation results will show that after 50 to 100 years much of the concrete is uncarbonated. The rate of carbonation will be very low after 30-40 years. Thus a major CO₂ uptake will take place when the concrete structures are demolished. Thus end use of demolished concrete, the degree of fragmentation and the environment where the demolished concrete is placed are of vital importance. Data needed are:

- Defined time frame for calculation of CO₂ uptake.
- Major areas of consumption.
- Major types of cement for the different areas of consumption.
- Estimation of area of exposure for different elements of concrete structures.
- Better data on the effect of cover and painting on concrete surfaces.
- Time before demolition of concrete constructions and products.
- End use of demolished concrete and environment end use of demolished concrete.
- More accurate data are also needed on the amount of remaining Ca ions in the silica gel. This can easily be determined by SEM/EDAX on different carbonated concretes.
- More accurate data on time between demolition, crushing and final use.

8 References

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Appendix 1. Examples of carbonation rates

The rate of carbonation can be theoretically calculated if we have all the relevant parameters. However, this is not the case. The carbonation rate must be estimated from test samples, from different exposure sites or from measured carbonation depth of existing structures. If we know carbonation rate for a concrete in a specific microenvironment and concrete quality the k -value for this specific concrete can be calculated.

Many calculations of carbonation rates have been performed as this is important for reinforcement corrosion and lifetime predictions.

One attempt has been made by CEB (Comité Euro-International du Béton). The work has been organised in CEB Task Group 5.1 and is reported in CEB No 238 (1997). The work aimed at finding means to calculate carbonation induced corrosion to be able to make a durability design. The calculations are based on Fick's second law to quantify the different variables. The rate of carbonation was used to find out when carbonation reaches reinforcement steel. This is basically the same type of calculation that is needed to calculate CO₂ uptake over time. The basis of the attempt is to find a value for concrete in a defined climatic condition and then add environmental factors to obtain the depth of carbonation after a certain time. The diffusion coefficient is adjusted by a constant that takes into account curing, micro climatic conditions, temperature. Such accurate values can be estimated for new constructions but in the attempt to calculate backwards from old construction and to be able to calculate a broad spectrum of new elements more rough estimates need to be done. In the CEB report data from and Hedenblad (1993), Wierig (1984), Kropp (1983) and unpublished data from "Institut für Bauphysik" in Holzkirchen (Germany) has been used.

Data from Wierig (1984) used in the CEB (1997) report calculates with data of concretes from an exposure site. The well-cured concrete has an effective w/c of 0.80 and the carbonation depth was measured after 16 years. The exposure site was in southern Germany. The climate can be regarded similar to southern Scandinavia but a little high for the northern more cold parts. From these data the k value can be calculated (CEB (1997)).

Indoor	18.5 mm	4.6 mm/ $\sqrt{\text{years}}$
Outdoor sheltered	13 mm	3.3/mm $\sqrt{\text{years}}$
Outdoor exposed	4 mm	1.0/mm $\sqrt{\text{years}}$

With data from Holzkirchen according to the CEB report a;

w/c of 0.7 gives

Outdoor sheltered 4,5 mm/ $\sqrt{\text{years}}$

w/c of 0.6 gives

Outdoor sheltered $3.1 \text{ mm}/\sqrt{\text{years}}$

Outdoor exposed $1.7 \text{ mm}/\sqrt{\text{years}}$

w/c of 0.5 gives

Outdoor sheltered $2.0 \text{ mm}/\sqrt{\text{years}}$

If we compare the carbonation rates presented in Wierig (1984) with that from Holzkirchen, both sites in southern Germany, the w/c 0.8 concrete should carbonate faster than the w/c 0.7 concrete, which is not the case. This shows the large scatter in data due to the many controlling parameters and the difficulty to get an accurate value for carbonation rates.

Currie (1986) examined carbonation depth of several types of concrete elements, in strength classes and in different types of climate. The data is compared with data from other investigations in Great Britain and in Germany. Prefabricated elements with an age of around 35 years give a depth of carbonation of around 10 mm. Most surfaces are classed as outdoor sheltered. The average κ -values were in the range of $1.5\text{-}2.5 \text{ mm}/\sqrt{\text{years}}$ and we can assume that the strength is more than 35 MPa. If we assume a w/c ratio of around 0.6 this is in accordance with the data from Holzkirchen. The study by Currie (1986) also includes old (54 years) concrete cast cylinders. The concrete can be regarded to show data for uncovered indoor concrete. Concrete with strength of around 40 MPa gives κ -values of around 3 and concrete with a strength of around 30 MPa gives κ -values of around 6. Carbonation measurements on old concrete structures give a large scatter but clear trends.

Tuutti (1982) compared different concrete qualities (w/c) in both outdoor sheltered and unsheltered concrete. The data comes from a combination of laboratory, literature data and cases from the CBI record.

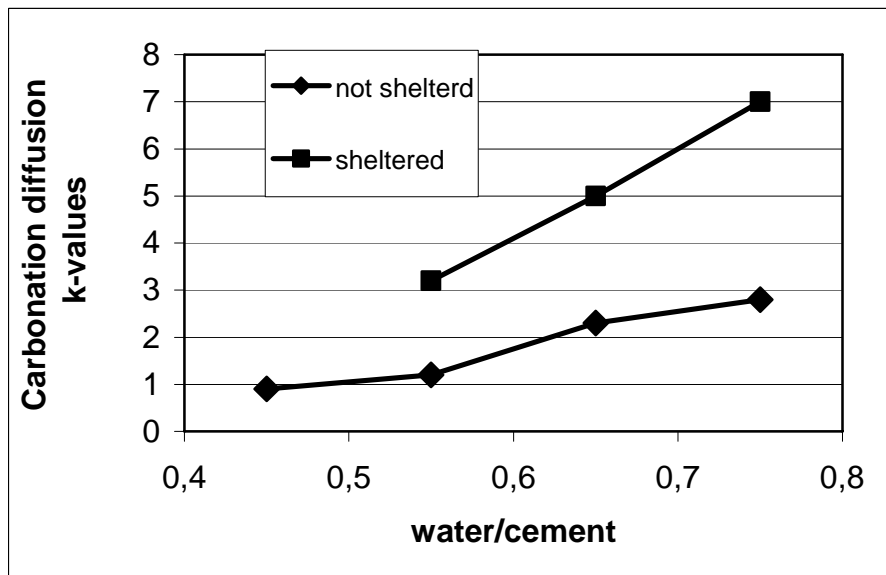


Figure 1. Relationship between carbonation rate and water cement ratio. The data has been taken from figure 23 in Tuutti (1982). It is upper boundary values from a data compilation.

Ali and Dunster (1998) in a BRE-report have investigated concretes with similar strength (C30) under different curing and environmental conditions. The results show that the curing regime is important but the climate is more important. The results also show that the carbonation rate goes up when the Portland cement is mixed with fly ash (Pfa) and/or granulated blast furnace slag (GBFS). The influence of GBFS and Pfa seem to be more accentuated in outdoor and laboratory conditions where the capillary system allows more gas transfer. Laboratory conditions can be assumed to be similar to indoor conditions. The data show that, in the laboratory or sheltered outdoors conditions fly ash and slag increases the carbonation rate by between 50 and 60 %. With outdoor exposed no difference can be noticed. The exposure time is, however, short and one can assume that the differences in carbonation rate will go down with time as the slag and fly ash concrete hydrate more slowly.

Table 1. Carbonation depth of C30 concrete under different environmental conditions and with different types of binder. In the Pfa mix the binder contains 30 % Pfa and in the slag mix the binder contains 50 % GBFS. The data are from Ali and Dunster (1998).

	C30 with pure PC concrete	C30 concrete with PC and fly ash	C30 concrete with PC and GBFS
Lab 20° 65 % RH	5.8 mm/ $\sqrt{\text{year}}$	9.6	8.2
Outdoor sheltered	3.8	6.2	6.2
Outdoor exposed	2.9	2.4	2.9

The data on the increases carbonation rate with blended cements is supported by other data from Meyer, Wierig and Husmann (1967).

A compilation of data of carbonation depth related to time is also presented in Parrot (1987). More data can be found in Richardsson (1988). From this it is obvious that there is a large scatter in the data. General trends can, however, be noticed and they are similar to the ones described above

Fukushima (1988) carried out a theoretical investigation of the influence of various factors on carbonation of concrete. Among other things he investigated the influence of amount of CO₂ on carbonation rate. It is quite clear, as expected, that it has a clear influence. According to his calculations an increase of the partial pressure of CO₂ from 0.03 to 0.06 will increase the carbonation rate 5 times. Thus the content has to be considered in industrial environments (chimneys etc). Moreover, indoor climate contains more CO₂ but this is included in the statistics from indoor climate. These data also indicate that the increase in CO₂ in the atmosphere that can be observed today will influence the CO₂ uptake

In a survey CBI has gone through its records of old consultant reports from 1990 to 1993. Often these contain both concrete quality, environment and carbonation depth. Cases are from garages, balconies, water towers, and different slabs. We tried to distinguish between wet, cyclic wet/dry, dry and outdoors sheltered concrete but it was very difficult to make a good classification according to the microclimate. For example a balcony could be in both categories depending on the position of the sampling. Almost all of the cases are from outdoor concrete and thus it is difficult to draw a line between dry and sheltered concrete. The general

trend is, however, clear. Concrete in wet microclimate carbonates the least while sheltered concrete carbonates the most.

Most of the concretes have strength between C25-35. In the figure below lines are drawn according to estimated k -values from Table 2 that is based on other data in this appendix.

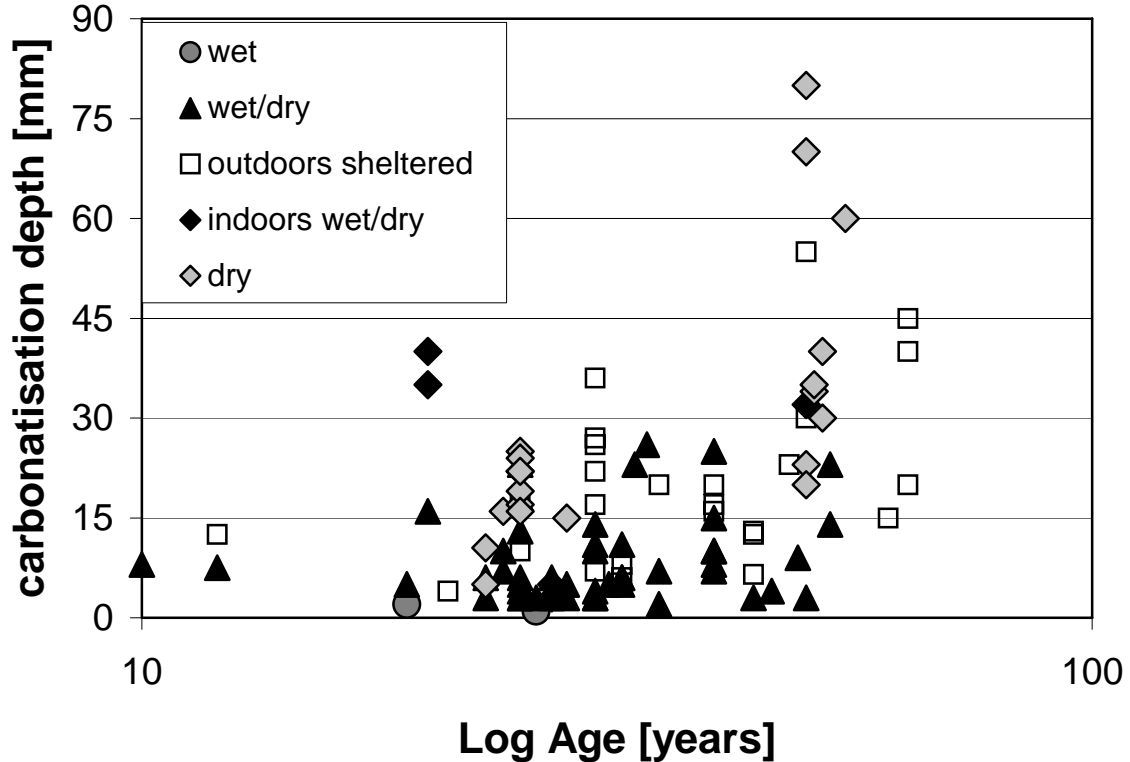


Figure 2. Carbonation depth from CBI consultant reports (119 samples). Most of the concrete is in strength class C 25-35. Years in log scale.

The data scatter is considerable but the general trends are clear, i.e. dry concrete carbonate faster than sheltered or wet concrete. Concrete with high strength carbonates more slowly concrete with low strength. The scattering in many cases is probably due to cover protection. This investigation like many of the others that have measured real elements shows that in the real world it is difficult to find absolute k -values.

Appendix 2. Figures and data needed for calculation of CO₂-uptake

To obtain a good calculation of CO₂uptake many parameters are needed. Thus simplifications are needed. Firstly it depends on the type of statistics that are available. The statistics do not show structural details but end user groups. Data that are available are based on the amount of cement that goes into prefabricated products and to ready-mix plants. Based on types of cement one can probably distinguish between house and infrastructure concrete. As regards infrastructure concrete one can probably find how much goes to bridges and marine structures etc. Other data can be split up into roads and cement products like concrete block pavements, bricks and tiles. It is probably also possible to find the amount of cement that goes to pipes, roof tiles etc.

To be able to perform a calculation we must however, first recognise the major consumption areas. When this is done the major consumption areas must be split up in details and then the CO₂uptake of these details must be synthesised into a general uptake of this type of structure/consumption. This is a work belongs to the other tasks. If this type of categorisation is made data have to be obtained about on concrete strength, type of cement and consumption from the past.

A2.1 General types of consumption areas

- Buildings
- Infrastructure
- Pavements
- Cement products like tiles tubes etc.

A2.2 Structural elements and details

- Pavements
- Blocks
- Elements
- Slabs, hollow core
- Slabs, massive
- Slabs on ground
- Pipes
- Tiles
- Columns/beams
- Bridges
- Marine structures

A2.3 Needed data and suggested divisions

- Strength class. < C15,C15-25,C25-35,>C35
- Type of binder CEM I, CEM II, CEM I with fly ash, CEM I with silica fume
- Amount of Portland clinker. Recalculate to amount of CEM I
- Amount of CaO in CEM I
- CO₂-Uptake

Environmental factors

- Outdoor exposed
- Outdoor sheltered
- Indoor
- Underground/buried
- Submerged

A2.4 Suggested data for carbonation rates

Carbonation rate in k -values for concrete surfaces with CEM 1 and naked concrete surfaces. Strength class in cylinder values (C).

Strength	< 15 MPa	15-20 MPa	25-35 MPa	> 35 MPa
Exposed	5 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$	1.5 mm/ $\sqrt{\text{year}}$	1 mm/ $\sqrt{\text{year}}$
Sheltered	10 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	4 mm/ $\sqrt{\text{year}}$	2.5 mm/ $\sqrt{\text{year}}$
Indoors	15 mm/ $\sqrt{\text{year}}$	9 mm/ $\sqrt{\text{year}}$	6 mm/ $\sqrt{\text{year}}$	3.5 mm/ $\sqrt{\text{year}}$
Wet	2 mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0,75 mm/ $\sqrt{\text{year}}$	0,5 mm/ $\sqrt{\text{year}}$
Buried	3 mm/ $\sqrt{\text{year}}$	1.5mm/ $\sqrt{\text{year}}$	1.0 mm/ $\sqrt{\text{year}}$	0.75mm/ $\sqrt{\text{year}}$

Correction values

Cover correction factors for cover, paint etc from chapter 5.1

- Indoor house concrete $k \times 0.7$
- Outdoor house concrete $k \times 0.9$

Binder correction factors based on strength classes. Percent in weight of binder from chapter 5.1

- 5-10 % silica fume $k \times 1.05$
- 10 % limestone $k \times 1.05$
- 20 % limestone $k \times 1.10$
- 10 % fly ash $k \times 1.05$
- 20 % fly ash $k \times 1.10$
- 40% fly ash $k \times 1.20$
- 20 % GBFS $k \times 1.10$
- 40 % GBFS $k \times 1.20$

Calculations of amount of CO₂.

$$\text{CO}_2 \text{ uptake} = a = 0.75 \times C \times \text{CaO} \times \frac{M_{\text{CO}_2}}{M_{\text{CaO}}} (\text{kg} / \text{m}^3)$$

0.75 amount of CaO carbonated (chapter 2)

C = Amount of Portland cement in concrete per m³

CaO = amount of CaO in cement (wt-%).

M = molar weight of oxide

This calculation will give the CO₂-uptake.

The exposure class is not always obvious and thus each detail/element must be examined and average values must be given.

To be able to calculate the CO₂ uptake from buildings an average building must be assumed. This means that information from single storey family houses to high rise building must be averaged. This can be based on the type of calculations performed above. But it has to be averaged so that we find how fast a building etc carbonates. If we can find the amount of concrete that has been used for buildings over the years and how fast it carbonates we only need the type of cement and the strength classes used.

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