The carbon uptake by carbonation of concrete structures – some remarks by perspective of TA

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Abstract

An issue which recently raised remarkable attention in both industry and politics with regard to CO_2-emissions of the cement industry is the uptake of CO_2 into concrete structures from the atmosphere due to weathering. Lobbyists urge to implement this overlooked sink of CO_2 within the global CO_2-balances. In this paper we examine the question whether the currently proposed methodology and database are sufficient for implementation. The experimental database is assessed to be doubtful due to inadequate testing. No reliable correlation of carbonation and age of buildings exist. Simple models are insufficient to allow a transfer in real buildings. A compensation of today's emissions with carbon that is sequestered by the existing building stock is implausible. The after-service life is assessed to be of higher importance. But the practicability and the economy of new procedures for enhanced carbonation of crushed concrete are uncertain. On the existing basis, the drafting of guidelines for IPCC appears to be very problematic. There are indications that a substantial fraction of CO_2 once emitted would remain within the atmosphere for thousands of years. Even if CO_2 is sequestered with a long-term delay, damages caused by extreme events cannot be retroactively reversed. The cement industry finds itself in a tricky situation. In the medium term, there is no serious alternative binder in sight and the realization conditions of CCS are unclear. For this reason, to the author's perspective, reinforced R&D in the field of radical innovations of low-CO_2-binders is strongly recommended.

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1. Introduction

Over the past 170 years, concrete, with Portland cement clinker as a main ingredient, evolved to be the most important core construction material worldwide. During the last decades, the global cement industry showed annual growth rates of 7% and more: Cement production rose from 1.16 billion t in the year 1990 to about 4.1 billion t in 2018 (see Figure 1) [USGS_2019].
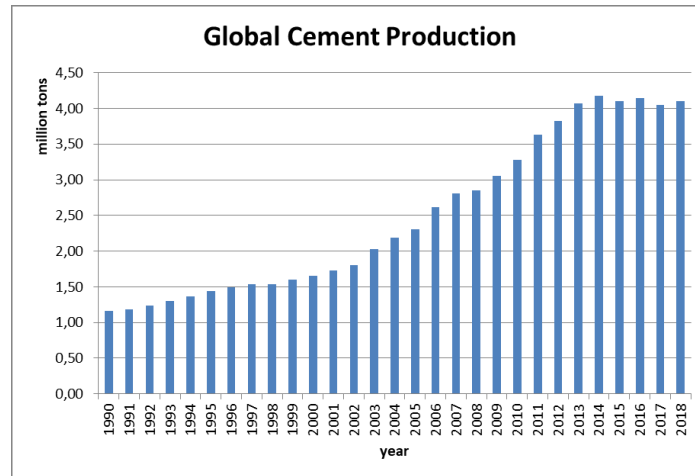

Fig. 1 Global cement production in the period 1990 -2018 [USGS_2019]

Cement manufacturing is associated with large process CO_2-emissions, originating from the calcination of carbonate-based raw materials (limestone) during corresponding clinker production. On the average about 0.52 t process CO_2 is liberated per ton of clinker in addition to CO_2 from fuels and power production (Andrew_2018; Achternbosch et al_2019). In the period from 1990 to 2016 global process emissions rose from 558 million tons to 1490 million tons [Andrew_2018]. Currently, process emissions alone contribute more than 4% to global man-made CO_2 [Achternbosch et al 2019], which from the perspective of the cement industry, are thought to be unavoidable (Leilac project_2019).

In recent years, the cement industry has made great efforts to minimize their carbon footprint. Unfortunately, the potential of measures within the conventional cement production are already largely exhausted. It is crucial that no real radical solutions are available in the medium term to reduce CO_2-emissions during production [Achternbosch et al_2018; Achternbosch et al_2019; Favier et al_2018]. The shortage of alternatives has strengthened those experts who are skeptical about the feasibility of any innovation beyond the Portland clinker paradigm. This, in the context of climate debate, in turn increases the pressure with regard to mitigation activities.

2. Problem definition – the revaluation of carbon uptake

2.1. History of discussion, Reception by cement industry

An issue which recently raised remarkable attention in both industry and politics with regard to CO_2 emissions of the cement industry is the uptake of CO_2 into concrete structures from the atmosphere due to weathering. In 2016 an elaborate study performed by an extensive research consortium emerged and attracted attention within the cement community [Xi et al_2016]. The study investigates the uptake not only on a global scale but also takes other types of cementitious materials like mortars and waste materials into account. The team describes the vast volume of historically consumed cement

available to absorb CO_2. They estimated the cumulated amount of CO_2 sequestered during the period 1930-2013 to 4.5 Gt of carbon which results in an offset of 43% of the process CO_2-emissions released from the manufacturing of cement in the same period. CO_2-emissions from fossil fuels during production are not included. They concluded that carbonation of cement-based structures during their life cycle represents an overlooked and large sink of CO_2. This estimation is based in particular on the assumption that mortar accounts for 30% of total global cement consumption in the period under consideration and that it is almost completely carbonated at the end of its life cycle.

According to the authors concrete, although having the main share (70%) of the total cement consumption contributes to the CO_2-uptake to a smaller extent: A cumulated average of 18% of the initial process CO_2-emissions (process-emissions) is assumed to be absorbed during service life, demolition and secondary use or disposal of pure concrete constructions.

Although there is no causal relationship between the emissions of producing cement plants and sequestration by historic concrete buildings, they deduct the amount of sequestered CO2 from the process emissions and state this figure as "net cement emission" [Xi et al_2016].

It is not astonishing that cement companies and associations emphasize the results of this study by following the line of argumentation in its entirety [VÖZ_2016, Cembureau_2019]. It is pointed out that there is a need for a change of perception with regard to cement. It is argued that in the past carbonation has only been assessed in terms of durability of structures. Carbonation would traditionally only imply negative connotations with regard to structural integrity [Cembureau_2019]. Now this issue is seen as a positive effect that would even improve the strength and quality of the structure. The high pressure on the industry to mitigate CO_2 results in the desire for a fast consideration of the CO_2-reducing effect. Therefore, lobbyists urge scientists to include the absorption of CO_2 by concrete in the calculation of global CO_2 emissions.

2.2. Subject of the investigation

Even though it is understandable that the cement industry is very interested in implementing the issue within the global CO_2-balancing, the question may be asked whether the currently proposed methodology with respect to databases, time-scales and allocation are sufficient for implementation. A key question is an assessment of the uncertainties within this complex issue and how to handle them. Is the proposed procedure really accurate and reliable? Is the scientific database sufficient and are all important results included in the procedure? Most conclusions are based on model calculations. Are the results transferable to large-scale conditions in real buildings?

The global balancing of the carbon cycle has the objective to obtain an instrument for the assessment of future climate related human activities. This objective can only be met if the individual contributions are calculated with highest accuracy. There is a risk that careful scientific validation will be dispensed and a simplificated idealized handling of the research field cement chemistry in the context of carbonation will lead to highly erroneous results.

2.3. Changing the perception of concrete: New EPD allows offset for carbon uptake

In June 2017 a European Standard DIN EN 16757:2017 has been released which provides additional requirements to set up Environmental Product Declarations (EPDs) for concrete and concrete elements [DIN EN_2017]. It details the rules for calculating the Life Cycle Inventory and the impact assessment on which the EPD is based. Optionally, the CO_2-assoziated with carbonation may be disclosed for each of the life cycle phases. If CO_2-absorption due to carbonation is not taken into account, this must be

documented in the EPD. Calculating carbonation requires various assumptions and a set of parameters. Annex BB of the standard provides a possible method to determine the carbon dioxide uptake due to carbonation in the different phases of the life cycle depending on the above parameters.

Relevant data is derived by a study of the Swedish Cement and Concrete Research Institute performed by B. Lagerblad [Lagerblad_2005]. This work has received the status of a reference study that compiles selected reports in concern to this issue but is based mainly on reports of CEB (Comité Euro-International du Béton). Roughly, the calculated extent of carbonation during service life can be interpreted to be in line with the study of Xi et al. in 2016. Beside the method proposed by Lagerblad, other methods have been worked out differing in complexity, assumptions, boundary conditions, approach, and used basics. DIN EN 16757:2017 allows the use of other calculation methods if they are clearly documented. Meanwhile EPDs of concrete exist, disclosing carbon uptake as offset. [Institut für Bauen und Umwelt ibu-epd_2018].

2.4. Integration of concrete as a sink in the global carbon cycle: Current status

At present the aspect of reabsorption of CO_2 by carbonation of concrete during its life cycle, including demolition and crushing is not systematically accounted for in global balancing of the carbon cycle notably the activities of Global Carbon Budget [GCP_2018] and IEA. The effect is relevant for the estimation of the category Fossil CO_2-emissions (E_{FF}) which also embraces by convention the cement process emissions. There are currently still reservations about adopting this issue. According to Global Carbon Project, the balance of these processes is not clear [GCP_2018].

The "2006 IPCC Guidelines for National Greenhouse Gas Inventories" regulates how emission-calculations are to be carried out in the framework of the Intergovernmental Panel on Climate Change (IPCC) [IPCC_2006]. The current version does not consider the effects of carbonation of concrete structures. The cement industry with reference among others to the ISO EN 16757 standard regards the knowledge base sufficient to recognize carbonation. Recently, the Swedish Environmental Research Institute IVL carried out a study co-financed by the Swedish Cement industry with the aim to work out background information and calculation models for IPCC implementation [ivl_2018]. In line with the approach established for the IPCC Guidelines, this study develops three different calculation methods (Tier 1, Tier 2 and Tier 3) with increased model complexity.

3. Methodology and Approach

In this study, we would like to make a first assessment of the effects of carbonation from perspective of Technology Assessment (TA) and cement chemistry. Methodologically, TA is specialized working with epistemologically precarious knowledge. Information and data on many objects of TA-investigation is basically uncertain and occasionally hardly available or of poor quality. System boundaries have to be defined on the basis of practicability. Reliable conclusions can only be drawn with simultaneous reference to their scope. TA basically tries to adopt a critical attitude towards one-sided trustfulness in models, numbers or in methods, as is repeatedly observed in disciplinary communities.

In this context, it should be noted that there are incomplete and partially controversial views on the kinetics, extent and spatial distribution of carbonation in concrete. The aim of TA is to promote objectification and to broaden the discussion by adding additional important points of view. The investigation is based on a literature review, interviews of cement experts and own expertise in cement chemistry.

4. Weathering and ageing of concrete – basics
4.1. Chemical and mineralogical characterization of young concrete

Concrete is made up of approximately 80% mineral aggregates by weight, which are glued together by the cement matrix. The weathering of young concrete mainly depends on the chemistry and phase inventory of the young matrix, its microstructure and the weathering environment (humidity, temperature, mechanical and chemical stress etc.). A hardened matrix made from Ordinary Portland Cement (OPC) essentially consists of $Ca(OH)_2$ (portlandite), an amorphous calcium silicate hydrate gel, (CSH) and two types of calcium aluminate ferrates, AFt and AFm. AFt and AFm differ in the amount of additional anions (e.g. sulphate, carbonate, hydroxide besides of aluminate and ferrate) in the structure. The pH in the young cement matrix is roughly 13 (Figure 2), i.e. it is extremely alkaline.

CSH has a complex chemical composition and can be described by the formula $m\ CaO*SiO_2*n\ H_2O$. The factor m is also referred to as molar ratio CaO/SiO_2 or C/S ratio. The C/S ratio observed for CSH in concrete varies between 2.3 and 1.2 [VDZ-Taschenbuch_2008]. A C/S ratio of about 1.7 is usually observed in OPC based young concrete ($C_{1.7}SH$). The mass of water (w) used in concrete formulations relative to the mass of cement (c), i.e. the w/c value is decisive for the composition of the hydrates formed. Lower w/c values apparently lead to phases with higher C/S ratios; CSH is then inseparably mixed with amorphous $Ca(OH)_2$.

4.2. General description of the carbonation process

Carbonation already starts during concrete processing, driven by the high pH value of the pore solution. Thus, minor amounts of calcite are always present in young concrete. In addition, special types of cement may contain ground limestone as main component. Quite often aggregates of concrete also comprise limestone or dolomite. It is therefore not possible to determine the carbonation rate of a concrete during its life cycle by simply analyzing the content of carbonates.

The carbonation reaction is catalyzed by the mixing water. Carbonic acid is generated at the wetted surface of open pores by the uptake of CO_2 from the air. The pH value of the pore solution decreases. Calcium is dissolved from the hardened cement paste and dissociates towards the surface, at first mainly from $Ca(OH)_2$. Dissolved calcium and carbonate ions precipitate as $CaCO_3$ in the open pore volume. In addition, excess water is formed. The carbonation rate strongly depends on the initial open porosity and humidity at the surface. The porosity is mainly influenced by the concrete recipe, especially by the w/c ratio and the quality of homogenization and compaction. With increasing age, the initial porosity may change dramatically. For instance, micro- and macro cracks open up and close, the latter mainly due to the precipitation of calcite, which in addition partly closes the initial porosity at all length scales by clogging (Morandeau et al. 2014). As a result, the overall diffusion rate decreases, such that the mobilization of calcium remains constant or even drops. However, dissolution and transport of calcium may also originate from other acids, e.g. acid rain. The same applies to acids from biological activity or agriculture. Dissolution by other acids diminishes the potential for precipitation of CO_2. A systematic review on literature related to the mechanisms of carbonation is given by Šavija et Luković_2016.

4.3. Phase changes in the carbonating cement matrix

Most studies in literature monitor carbonation by the associated change in pH or the conversion of portlandite, $Ca(OH)_2$ to calcite, which can readily be observed with x-ray diffraction (XRD) and thermal analysis (TA). As long as $Ca(OH)_2$ – as a crystalline phase or disordered in layers of $C_{1.7}SH$ - is accessible

by pore water through open pores this phase is selectively dissolved. The pH is buffered above 12,4. Dissolution of disordered $Ca(OH)_2$ in amorphous calcium silicate hydrate gel $C_{1,7}SH$ already changes its structure, composition and specific surface. With decreasing pH the amount and composition of all other hydrate phases present in the cement matrix, namely the calcium aluminate ferrates, Aft and Afm change too. The calcium content of the CSH further decreases. Phase changes and calcite precipitation result in local inhomogeneities on the micrometer to nanometer scale. Samples with an average pH of the pore solution below 12 usually still contain closed regions in equilibrium with $Ca(OH)_2$ (Figure 2). Further dissolution of calcium results in CSH with a lower C/S ratio but a higher structural order, $C_{1,25}SH$ until at pH of about 11 in the capillary pore system a CSH with an average composition of C_1SH is formed, which is often separated by a highly polymerized dense silica-gel from the open capillary porosity. In addition, AFm and mostly $CaCO_3$ are present. During service life, this state is reached very rarely.
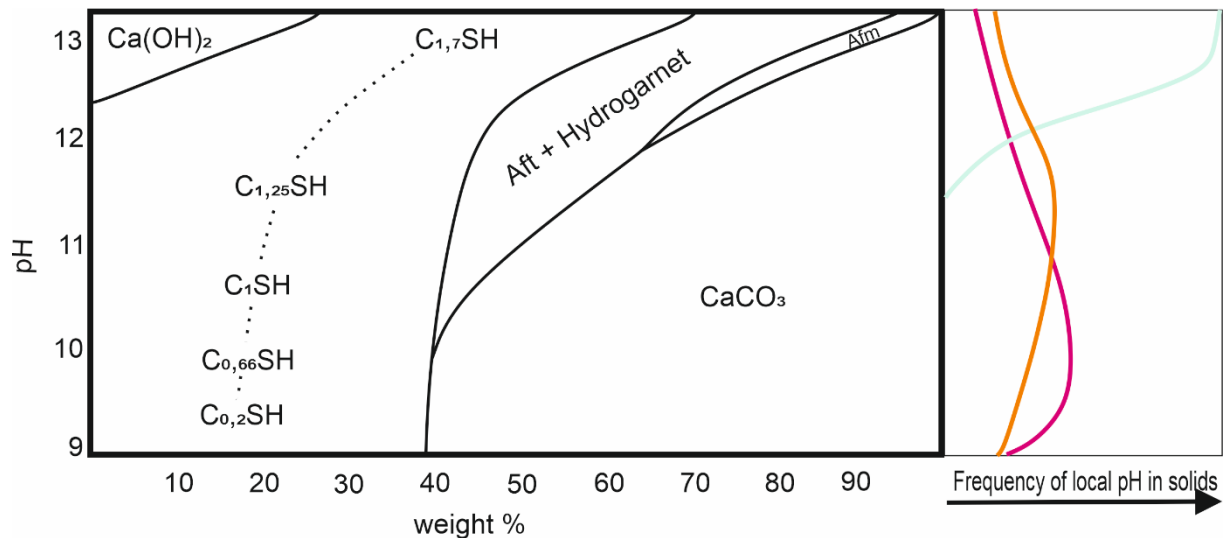

Fig. 2 Tentative average phase inventory of the cement matrix in concrete made from OPC during diffusion-controlled carbonation, plotted as a function of the pH value in equilibrium with the corresponding solids. Sound concrete (green) is dominated by portlandite, CSH, Aft and AFm. Partly carbonated (orange) and even heavily carbonated regions (red) do usually still contain closed pores in equilibrium with $Ca(OH)_2$. Their abundance decreases with increasing carbonation [Achternbosch et al_2003, adapted].

If carbonation further proceeds, porosity, grain size, and the crystal structure of the phases present are further modified. Local inhomogenity increases. Mechanical and chemical weathering on the new surfaces may accelerate the access of acids. As a consequence, the classical model of hardened cement paste weathering predicts a complete decomposition of C_1SH into SiO_2 and $CaCO_3$ under complete release of the incorporated trace elements. AFt and the hydrogarnet phase decompose. Modern research [eg. Sevelsted et al. 2015] however demonstrates, that the decalcification of C_1SH during normal carbonation at least proceeds down to $C_{0.66}SH$, before ultimately a phase with a zeolite-like structure $C_{0.2}SH$ (faujasite gel) is formed. The $C_{0.66}SH$ phase still has the basic structure and cohesive properties typical for CSH in cement. The stepwise decalcification of CSH during carbonation has been incorporated in thermodynamic databases (Kulik_2011) and used e.g. by Weerdt et al_2019 to model carbonation of mortar.

C_1SH (tobermorite gel) → $C_{0.66}SH$ (gyrolith gel) → $C_{0.2}SH$ (faujasite gel)
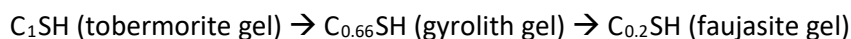
CSH with a C/S ratio of below 1 and hydrogarnet are still present in roman concrete used to build ancient baths after 1800 years [Thomassin et al_1992]. Thus apart from the $Ca(OH)_2$ buffer, with the CSH-phases another buffer system exists in the cement system, which is effective between pH 12 and about 9. Local access of acid can lead to precipitation of dense silica gels at any time. Moreover, independent of carbonation the structure of calcium silicate hydrate gels also changes with increasing age. Both aging and carbonation [Sevelsted et al_2015] may result in shrinkage and microcracks. The individual processes are not known in detail. According to Kulhawy research points to complex behavior in the CSH-phases with regard to carbonation issues [Kulhawy_2002]. Analytic investigations are extremely demanding. Since the current knowledge of the CSH phases is still assessed to be rudimentary [Galan et al_2015], the question arises whether the knowledge is sufficient to draw conclusions from simplistic approximations with reliable results.

Today, despite of massive progress in thermodynamic data, crucial kinetic data is still not available. Given these data the carbonation of a finely ground cement matrix under laboratory conditions could be modelled ab initio. The carbonation of concrete however is additionally ruled by the interference of chemical transport reactions with microstructure and porosity. Thus for a fundamental approach a spatially resolved multi-scale 3D modelling would be necessary - with a resolution that spans from a few nm, the size of CSH particles up to mm, the size of macro cracks. In order to describe young cement pastes such models are currently being developed. In summary, it must be emphasized that modelling the carbonation of concrete today requires strong simplifications, which only allow for a very limited accuracy.

5. Discussion of carbonation assessment during service life

5.1. Bottom-up-approaches

5.1.1. Introduction

In 2005 a series of reports initiated by the Danish Technological Institute argued that the natural CO_2-uptake of concrete during life time would be undervalued in global and national CO_2-balancing [Lagerblad_2005; Engelsen et al_2005; Jonsson_2005; Kjellsen et al_2005; Pommer et al_2005].

The investigations culminated in the mentioned study of Xi et al. Even though the assumption seems to force multitudes of new investigations based on advanced model calculations and accelerated carbonation testing programs, relatively few studies have been published so far. This calls for a critical discourse on the studies presented by Xi et al. and others in the same context.

5.1.2. Experimental Quantification of Carbonation

Degree of carbonation, difficulties of determination with respect to homogeneity of concrete in different length and time scales

In order to quantify the CO_2-uptake of concrete during life time Lagerblad and co-workers estimated the final degrees of carbonation after a 100 years natural weathering of a variety of cement based materials under varying weathering conditions. They defined a parameter, the "degree of carbonation" in order to describe the expected final proportion of sequestered CO_2 by a thin concrete slab that has been fully exposed to air for a 100 years relative to the related process emissions of the contained cement during its manufacturing.

Concrete itself is an extremely inhomogeneous material with varying cement contents, degrees of hydration, mechanical strength, porosity, crack density etc. Therefore the "degree of carbonation"

varies on different length and time scales even in one sample (Figure 2). With respect to length scales the opening and closing of porosity in the macro, micro and nanometer scale may result in degrees of carbonation from 0 to 100%, independent from time scales.

In order to experimentally determine valid degrees of carbonation it is therefore of highest importance that the amount of newly formed carbonate is truly measured. The quantification of carbonate cannot be replaced by pH measurements based on the wrong assumption that below a certain average pH in a sample all calcium is present as $CaCO_3$. The strong inhomogeneity of the pH has already been discussed in chapter 4.3. Thus in order to account for the inhomogeneity it would be necessary to measure the pH with a spatial resolution matching the observed particle sizes in the nm range. The determination of the pH value further neglects the effect of other acids that may have affected the respective sample during weathering.

For each sample the determination of the carbonated reactive CaO requires a large number of measurements to be statistically significant. In addition, the average total content of reactive calcium oxide at the beginning of its service life must be determined by probing a statistically significant number of points of the respective sample, that have not been affected by carbonation or other forms of chemical weathering.

Experimental validation of carbonation

The exact determination of the degree of carbonation is only possible, if a concrete volume with an unaffected core is present. The carbonate content in this core, which may originate from e.g. the addition of limestone in composite cements (see chapter 4.2) must be carefully analyzed. Unfortunately amorphous calcium carbonate phases are quite common, which makes a combination of e.g. XRD and TA with IR-detection of CO_2 necessary. The derived reference content of carbonate can be compared to the carbonate content in representative volumes of concrete affected by carbonation. To do so, analytical methods which allow for a high spatial resolution, e.g. micro-Raman spectroscopy or densiometry have to be combined with quantitative measurements. In addition, the average clinker content, its spatial distribution and composition, additions of supplementary materials like fly ash or slags, type of aggregates, w/c ratio, climate during weathering etc. have to be known to draw general conclusions on the rate of carbonation for the respective conditions.

Unfortunately, investigations on carbonation that meet this standard are hardly known. Even the effect of the most common cement types on the carbonation of concretes is not clear. For limestone portland cements for example drying shrinkage and carbonation depths show mixed results, in some cases being increased and in some decreased when compared to control OPC. The differences are of limited practical significance in the context of overall concrete mix variations [Hawkins et al_2003].

Accelerated Testing

Because of the extreme time-consuming tests and high analytical effort required to investigate the carbonation of real aged concretes under controlled conditions, simpler methods are needed, especially for quality control. Thus, empirical tests have been developed, which shall mimic the carbonation during long term weathering of concrete in a practicable time. For this purpose, accelerated conditions (elevated temperatures, higher CO_2-concentrations, application of other strong acids, complexing agents) are used. It is important to note that the decalcification especially of CSH involves kinetically slow reactions. Therefore, if these phases are exposed to higher concentrations of acid, e.g. CO_2, immediate dissolution of calcium takes place without formation of intermediate products that occur in real weathering of concretes. The CSH buffer is "run over". Conventional

laboratory tests that simulate weathering by the addition of acids (availability tests) therefore represent "worst case" scenarios – which is completely adequate for a quality check, but does not allow predictions of their behavior in the real world. Changes in the microstructure, cracking and 3D-enclosement of calcium rich minerals are not reflected adequately.

Results from accelerated carbonation tests have been used to predict long-term carbonation behavior, but there is no general agreement on how to extrapolate from accelerated test conditions to real performance [Sanjuán et al_2003; Ishida et al_2004; Neves et al_2013]. In laboratory, too, simplifications must be accepted, even if efforts are made to take relevant influencing factors into account as far as possible. In many cases poor correlation between natural and accelerated carbonation can be found based on data from real structures, even for any given environmental exposure class, if different exposure classes are considered and especially if the phenolphthalein test that probes the pH (see following chapter) is used for real structures [Ekolu_2016]. There is no generally applicable mathematical relationship between an accelerated carbonation test and natural carbonation [Ekolu_2016]. This is not astonishing, as the mass transport properties of laboratory specimens and structural elements differ, as do the CO_2-concentration of accelerated testing and natural exposure conditions [Neves et al_2013]. Morandeau et al. [2014] tried to avoid the reported unrealistic effects of accelerated carbonation on the reaction path [Sanjuán et al_2003]. Thus they reduced the 50% CO_2-atmosphere commonly used in France for accelerated carbonation to 10%.
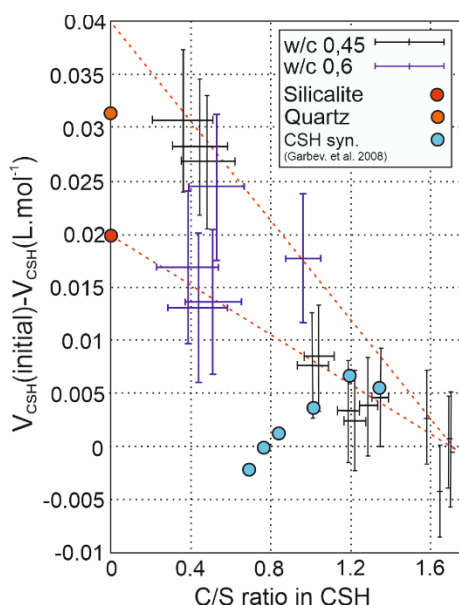
Fig. 3 Change of specific volume of CSH during decalcification in accelerated carbonation experiments (blue and black bares represent samples with different water cement ratios [Morandeau et al_2014]) compared to synthetic experiments [Garbev et al_2008]. The observed difference is interpreted as decomposition of CSH to silica and $CaCO_3$ during accelerated carbonation. Orange dot: a high density silica phase comparable to quartz forms in low w/c low porosity samples. Red dot: A low density silica phase comparable to silicalite forms in high w/c and high porosity samples. All volumes are normalized to 1 mole of silicon in CSH or silica.

A comparison of their data with experimentally measured volume changes in synthetic CSH phases with different C/S ratio [Garbev et al_2008] reveals, that nevertheless CSH in their experiments behaves different from what is expected for normal weathering conditions. As figure 3 demonstrates, the specific volume of CSH with a C/S near 1 should increase upon further decalcification during normal weathering (blue dots). In the accelerated carbonation experiments in contrast the specific volume of CSH seems to decrease. This contradiction is reasonably explained, if CSH decomposes to a silica phase with variable density (red and orange dots) and calcite during the accelerated test, which proves a completely different reaction path. As already mentioned in chapter 4 CSH with a C/S ratio of below 1 and hydrogarnet is still present in roman concrete used to build ancient baths after 1800 years [Thomassin et al_1992]. Interestingly these concretes have been in direct contact with hot CO_2-rich combustion gases during 100 years of service life, as they show a high sulfur content, which resembles an ancient accelerated carbonation test. With respect to modern accelerated carbonation a comparison of the models with in-situ-measurements is desired [Benitez et al_2019].

Staining test

An additional source of errors is the use of pH-indicators like phenolphthalein as staining to probe the pH in connected macro- and mesopores. This method measures a steady state between acid diffusion and pore connectivity. It therefore characterizes the local pore solution in disequilibrium with the surrounding solids. Nevertheless, it is the common method to measure the depth of carbonation of real concrete structures. The indicator is dissolved in an aqueous and alcoholic solution and sprayed onto the concrete surface. It is turning red in the non-carbonated, highly alkaline pore solution (i.e. pH value > 9) (Figure 4). Pore solutions in carbonated environments with a pH-value below 9 remain uncolored.
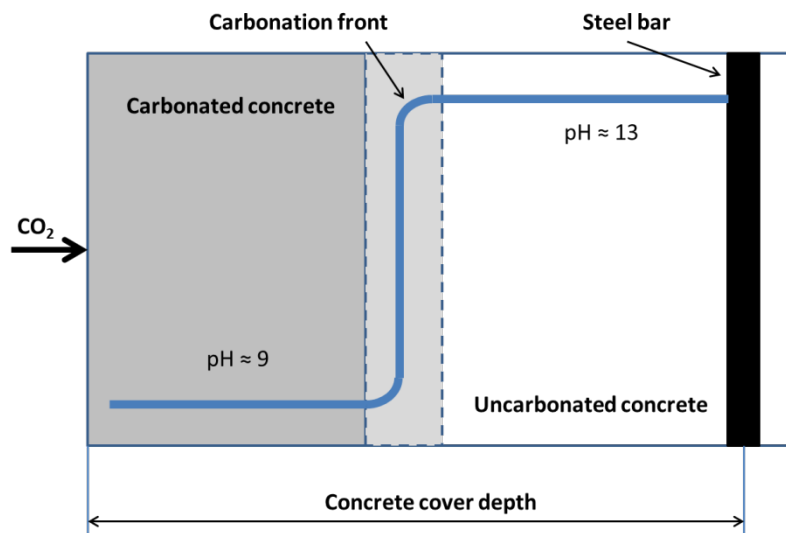

Fig. 4 Scheme of pH-change within concrete due to carbonation

Therefore, the test gives only information about the propagation of the pH-value in solution but no direct information about the carbonation depth. Gel pores in C-S-H or other closed porosity is not affected at all. Capillary pores up to an unknown diameter may contain not enough water to result in any visible staining. Regions with pH between 9 and 12 are characterized as uncarbonated although the effect is not clearly identified if carbonation only partially occurs or if carbonation occurs but with pH beyond the scope changeable by indicator. The test doesn´t stain CSH and the aluminates. C-S-H phases are generally difficult to classify with conventional methods as they are largely X-ray-amorphous.

The application of staining tests for quantitative measurements has been subject of critics. Research carried out to assess the depth of concrete carbonation show that the phenolphthalein indicator provides a poor estimate of the real concrete carbonation. [Kulhawy_2002; Hammer_2007; Thiéry et al_2011; Galan et al_2010; Pacheco Torgal et al_2012]. As a consequence, other testing procedures have been proposed [Chang et al_2006, Hammer_2007]. Villain et al_2007 compared thermo-gravimetry, chemical analysis (CA) and gamma-densimetry to assess carbonation profiles.

Evaluation of test procedures

A review of the relevant literature reveals many examples of in-situ measurements that give a large variation in carbonation depth on real structures for a given year of operation. Sometimes contradictory results on the same object of investigation can be found. For example, data from Alexander et al_2007 and Elgalhud et al_2017 show a scattering of the carbonation depth by a factor

of 15 to 20 for the same operating year. To demonstrate this issue, we additionally present correlations of carbonation depths with service life years for sheltered and unsheltered concrete performed by Benitez et al_2019, Lagerblad_2005 (according to CBI consultant reports), Janotkaa et al_2018, and Liang et al_2013 (Figure 5). In most of these investigations, the phenolphthalein test was used. The examples show the difficulty to derive time dependency. Other research on real structures indicates that any correlation is nearly impossible: Carbonation may progress differently at different areas of the same component under identical exposure conditions and for different components of the same building. This results in statistically different maximum carbonation depths, although the exposure time was exactly the same [Medeiros-Junior et al_2015].
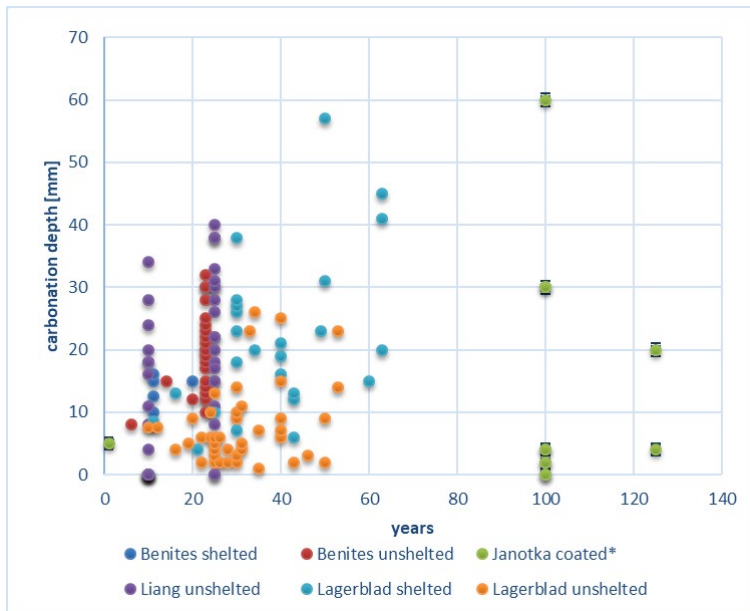

Fig. 5 Examples of the correlation of carbonation depths with service life years; data from Benitez et al_2019; Lagerblad_2005 (according CBI consultant reports); Janotkaa et al_2018; Liang et al_2013; most of the concrete C25/C35; *: plaster coated

Furthermore, especially for the cases of empirical examinations, there is mostly no or very unreliable information at hand which kind of cement, which cement quantity and which w/c ratio was used during construction in the past. Qualitatively inferior concrete with a high w/c value naturally carbonates faster.

In addition, it cannot be excluded that a great deal of the "empical" data corresponds to damage cases - from cases that can be classified falling outside the standard. Benitez et al_2019 for example analyzed 206 samples with a mean value of carbonation depth of 16.5 mm with a standard deviation of 7.25 mm by 25-30 years of service life. Analysis shows a large share of CO_2-corrosion due to insufficient cover thickness of concrete in the considered RC-structures. Common defects and damage to buildings have their cause before service life. If structural damage occurs, extreme carbonation depth are observed and reported, which are therefore statistically overrepresented in published data. An evaluation of damage by the building supervisory authorities revealed areas of cause with the following breakdown [Thienel_2017]:

• Design phase 15%,

• construction 45%,

• use 40 %.

Depending on the area of investigation or the objective, the scattering range is large. For example, in the case of industrial enterprises, the area of origin of the use phase is to be set much higher [Thienel_2017]. Without wanting to over-interpret these results, errors during execution at the construction site can strongly influence the results regarding the carbonation depth.

5.1.3. Modelling of damage caused by carbonation weathering

Carbonation has been known and studied for a long time with regard to damage of buildings by destruction of construction materials from the surface due to chemical or electrochemical reaction. In this context, carbonation is generally regarded as a *deterioration mechanism* for concrete [Zhang et al_2017]. The main binding component of cement, CSH is believed to decalcify, eventually becoming a silica gel (with zeolite-type structure) in the process and losing its binding capability as a consequence. Carbonation also induces an increasing vulnerability of embedded reinforcing steel to corrosion. The recently expressed view of carbonation as a positive effect, masks out the fact that carbonation lowers the pH in the paste matrix and therefore clearly increases steel corrosion in reinforced concrete (RC) - structures [Ekolu_2016].

The deleterious effect of atmospheric CO_2 on modern concretes and mortars is known as 'weathering carbonation'. In this context, carbonation has been extensively investigated. Laboratory studies have been conducted on hardened cement pastes and concretes (hydrated for 28 days or longer). Accelerated carbonation is subject to mimic long-term weathering. [Zhang et al_2017]. Many models of corrosion by carbonation and chloride with the aim to build up modeling for damage prediction have been published in the past. For details in this issue we refer to [Rostásy et al_1992, Müller et al_2011, fib_34_2006]. In addition, extensive literature on multi scale modelling of carbonation and its mechanical effects have been published. Unfortunately, despite of all these efforts the accuracy of predictive models on the macroscale in real life is very limited. The extent to which natural carbonation has an effect in the long-term on real, properly constructed concrete buildings is a matter of differing opinions and changing perception. This is in agreement with a more general assessment that there exists neither comprehensive data nor appropriate technologies concerning such a variety of deterioration factors (including carbonation) and phenomena, and further the method for the evaluation of the structural soundness of a carbonated structure is not yet fully established [Lee et al_2012].

Rough estimation of the maximum penetration depth of corrosive solutions in reinforced concrete for practical purposes: The root of time law model

The common model to predict the penetration depth of corrosive solutions initially proposed by Tuutti [Tuutti_1982] is based on the diffusion law assuming that the diffusion rate e.g. of carbonate is proportional to the square root of the time of exposure to CO_2:

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

In this equation x is the carbonation depth (mm); k is the carbonation coefficient (mm/year$^{1/2}$); and t is the exposure time to CO_2 (year). The carbonation coefficient k takes several relevant parameters into account assuming that these parameters are constant: the CO_2-concentration, the amount of CO_2 required for carbonation of a specific volume of concrete, and the diffusion coefficient for CO_2 through carbonated concrete.

5.1.4. Estimation of the sequestration of CO_2 by concrete by Lagerblad

In 2005 Lagerblad argued, that it is possible to estimate the sequestration of CO_2 by concrete by multiplying the estimated carbonation depth with an estimated degree of carbonation [Lagerblad_2005]. The carbonation depth is calculated based on the root of time law.

The most important additional variable used in the study mentioned above is the degree of carbonation D_c of a specific volume in a concrete structure. It refers to the hydrated cement matrix and is defined as the ratio of carbonated reactive CaO relative to the total content of reactive calcium oxide at the beginning of its service life. In practice an average degree of carbonation after 100 years is estimated for clusters of materials. Clustering depends e.g. on initial compressive strength and weathering conditions. Irrespective whether the existing data permits the specification of degrees of carbonation for the respective clusters, the question arises if the degree of carbonation can be determined exactly and reproducibly for individual samples.

The discussion of this issue needs some explanation. During cement hydration, besides the formation of CSH, half of the cement is transformed into calcium aluminate hydrates and calcium hydroxide (see chapter 4). The latter is formed from Ca_3SiO_5 and Ca_2SiO_5 according to the following equations [Neubauer et al_2007]:

$$Ca_3SiO_5 + 3\ H_2O \rightarrow Ca_{1,7}SiO_3{\cdot}H_2O + 1,3\ Ca(OH)_2$$

$$Ca_2SiO_4 + 2\ H_2O \rightarrow Ca_{1,7}SiO_3{\cdot}H_2O + 0,3\ Ca(OH)_2$$
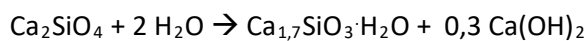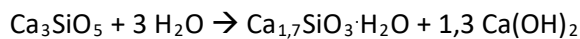
According to Taylor (Taylor_1990), one ton of clinker contains about 662 kg CaO. Based on this data it can be assessed that during hydration 228 kg CaO (34 w-%) may be transformed into portlandite (CH), and 355 kg of CaO (57 w-%) into CSH-phases (see table 1, chapter 4). Other clinker phases in total contain 79 kg CaO (12 w-%). However, the values obtained with this calculation method often deviate from the actual composition of cements or clinkers. Therefore, these are only guide values.

Table 1: CaO-content in calcium silicate and other phases of clinker and in the products of cement hydration portlandite (CH), CSH-gel and others. In addition, the corresponding CO_2-amounts are given. All data per ton of clinker.

per ton of clinker	kg phases	kg CaO	kg CaO in CH	kg CaO in CSH	kg CaO in others
Ca_3SiO_5	673	496	215	281	
Ca_2SiO_4	133	87	13	74	
other cl. Phases	194	79			79
Total	**1000**	**662**	**228**	**355**	**79**
theor. CO_2-uptake		520	179	278	62

The degree of carbonation must, of course, be related to a limited period of weathering. For a given time interval it can only be estimated with respect to the concretes composition and structure and the assumed (dynamic) weathering conditions. The less specific the knowledge about these individual parameters is, the more conservative the degree of carbonation must be estimated.

Lagerblad assumes that all calcium from the CH, half of the calcium from the CSH and all calcium from the AFm/Aft-phases is transformed to calcium carbonate (CC). Roughly 25% of the CaO of the original cement remains uncarbonated. Throughout his paper, he regularly considers a period of interest of 50 to 100 years. He argues that the stabilities of ettringite and monosulphate at different pH were studied by Gabrilová et al_1991. Based on potentiometric measurements of a dispersed solid phase in aqueous solution, they concluded that monosulphate is unstable below pH 11.6 and ettringite below pH 10.7.

These and other measurements of phase equilibria reflect thermodynamic stabilities but disregard the factor time (kinetics, chapter 4). Lagerblad agrees that the process of passing a shell of already carbonated concrete is complex. Nevertheless, he simply assumes, that within 50 to 100 years due to natural weathering of the cement matrix an average carbonation level is reached which is roughly equivalent to a thermodynamic equilibrium at pH 10.

The estimation by Lagerblad that 25% of the CaO in concrete remain uncarbonated is the basis for the 75% degree of carbonation (Dc) given in the European standard EN 16757. The standard differentiates infrastructure from buildings, regularly wet from mainly dry exposure, as well as indoor, outdoor and soil-covered conditions. For outdoor, the assumed values for D_C even range between 75 and 85%.

Lagerblad's estimation of the degree of carbonation was adjusted several times by other research groups. Researchers of ETH who first adopted this approximation [Nygard et al_2012] revised it and use a value of 50% in a recent study [Leemann et al_2018]. And as Stripple et al_2018 even agree 75% is accordingly a value that, for the bulk of concrete, takes a long time to achieve, so in spite of the long history of use, there are probably still only small amounts of concrete that have reached this status [ivl_2018].

Indoor concrete is exposed to higher temperatures than outdoor concrete in northern countries. It is assumed that a higher temperature results in a higher rate of carbonation. The carbonation rates used by Lagerblad mostly come from empirical data and are taken into account in the k-values. For k-values and the degree of carbonation (D_c) see table 2. Very high k-values are estimated particularly with regard to coatings and coverings of concrete. There is no consensus in science on the question of whether these layers hinder or favor carbonation. Thus, there is currently no basis for taking coatings into account in the calculations for CO_2-uptake.

Table 2: k- and D_c-values used to calculate the carbonation depth of selected concrete structures, depending on strength values of concrete and environmental exposition. Data based on [EN 16757]; own representation.

concrete strength	< 15 MPa	15-20 MPa	25-35 MPa	>35 MPa	degree of carbonation (D_c)
parameter	k-factor in mm/a				%
civil engineering					
unsheltered from rain		2.7	1.6	1.1	85
sheltered from rain		6.6	4.4	2.7	75
building		1.1	0.8	0.5	85
outside					
unsheltered from rain	5.5	2.7	1.6	1.1	85
sheltered from rain	11	6.6	4.4	2.7	75
inside dry					
coated	11.6	6.9	4.6	2.7	40
uncoated	16.5	9.9	6.6	3.8	40

Maries pointed out that 'the extent of sequestration of carbon by cement-containing materials has been calculated from compositional data and exposure conditions (rather than actually measured), then mathematically modelled making various assumptions. There appears to have been little field measurement to support the calculations' [Allen_2017].

Simplifications and related errors in time law model

The quantification of sequestered carbon based on the root t law is viewed very critically by some authors [Neves et al_2013]. The diffusion law is only valid for special conditions. In real exposure conditions, the CO_2-concentration is not constant over time, the diffusion coefficient is sensitive to the relative humidity which usually results in dry–wet cycles and the amount of CO_2 required to carbonate a unit volume of concrete depends on the amount of CO_2 available. Thus, the diffusion model must be adapted to the actual environmental onsite conditions and to specific concrete properties, which strongly change over time. Advanced models consider the influence of dry–wet cycles and modify the exponent of time to less than 0.5 as its action slows the carbonation rate. Other models incorporate the effect of dry–wet cycles into the carbonation coefficient [Neves et al_2013]. When cement with mineral additions is used, the carbonation resistance of mortar and concrete may be decreased [Cemsuisse 2018]. Some studies have shown that there are other factors that influence the kinetics of carbonation reactions. In this context, very elaborate models have been performed to minimize the shortcomings [e.g. Ta et al_2016]. As Lagerblad states additional uptake from undamaged surfaces after 50-100 years can almost be neglected. This statement counteracts the meaning of the root t law which assumes that the period of 50-100 years has a share of 30% on carbonation.

As already stated, neither concrete nor the cement matrix are homogeneous materials and possess a heterogenic microstructure and texture. Mass transport property disparities arise from different placing, compacting and curing [Neves et al_2013]. The impact of carbonation may engender important changes of the microstructure (porosity, pore size distribution, moisture content, connectivity, specific surface area) and is still a subject of research and even debate [Morandeau et al_2014].

A study of Galan et al. [2015] indicates that there exist certain regimes in which calcium carbonate films can form spontaneously which are remarkably effective in limiting diffusion of calcium hydroxide from cement and in protecting further carbonation of substrate portlandite. CSH phases may contribute to the establishment of protective surface layers. Therefore core-shells of $CaCO_3$ which inhibit further carbonation cannot be excluded. It is observed that the porosity of concrete decreases due to the higher molar volume of carbonation products in comparison to the volume of hydrates [Bouchaala et al_2011]. It is obvious that the observed decrease in porosity cannot only be due to CH carbonation. As a matter of fact, CSH carbonation may significantly contribute to this evolution [Morandeau et al_2014]. Many researchers agree on a complex decalcification-polymerization process of the CSH and the formation of amorphous dense rims of silica gel. The change in the volume of solid phases is complex and explains the difficulty to quantify with enough accuracy the evolution of porosity induced by CSH carbonation. The formation of dense silica phases will nearly stop diffusion, whereas zeolite structures can easily be passed. In the presence of high alkali contents silica gels may even swell and completely destroy the concrete (alkali-silica reaction).

It is argued [Lagerblad_2005] that the formed calcium carbonate would be porous but the source mentioned for it is not clear [Diamond_2000]. Furtheron it is assumed that the calcium carbonate precipitates near the CSH and influences the gel porosity to a greater extent than the capillary porosity. But this too does not seem to be an experimentally verified conclusion. Concerning the influence of carbonation on the pore size distribution of cement-based materials, the limited data which were

published in the scientific literature do not show a real consensus [Morandeau et al_2014]. With regard to the change in volume of capillary pores, different results exist [Pihlajavaara et al_1974; Thiéry et al_2011].

All investigations are performed on laboratory samples and mostly under accelerated conditions. In view of the differences between the structures of accelerated CO_2-carbonated samples and air-carbonated structures, caution should be exercised in interpreting the results of accelerated carbonation tests [Groves et al_1991]. Under natural conditions, experiments suggest that the influence of the carbonation of CSH phases might become even smaller because of the worse accessibility of carbon dioxide to CSH and the possibly lesser amount of CSH available in the concrete (owing to uncomplete hydration) [Peter et al_2008].

Against this background, the question of the applicability of the root time law on carbon sequestration can only be answered conservatively. A conventional diffusion model does not match natural carbonation in real structures. To our view the validity of the root time law is restricted to simplified and carefully controlled laboratory conditions. The transferability of laboratory results to buildings is highly problematic. The statement that the methods used in different countries are all based on the well-accepted and documented carbonation rate model of square root of time dependency [Stripple et al_2018] is therefore incorrect.

Aspects affecting the transferability of time series on future service life

There is a broad agreement that carbonation depends on the composition of concrete in terms of the w/c ratio and compressive strength, maturity and porosity. Lower w/c or water to binder ratios and high degree of hydration respectively result in denser concrete with a lower porosity. As a consequence, the carbonation rate will be reduced. It can be strongly assumed that concrete using cement with strength classes equal to or higher than 32,5 show relatively low carbonation rates [Lagerblad_2005]. Locher assumes for perfectly processed concrete a carbonation depth of only a few millimeters for C35/45 concrete for 30 years of service life (Locher_2006). This assessment is confirmed by own face-to face interviews with researches in CSH-mineralogy and chemistry of public research institutes. Many experts show a more skeptical view on the transferability and representativeness of laboratory-based and empirical studies on real structures. In the case of modern concrete structures, they doubt that carbonation really penetrates deeper than a few millimeters into the structures despite the fact that pores are closed and clogged.

In the years 70s to 80s, the formulation of concretes has changed significantly (new superplasticizer, finer grinding of cements, generally greatly reduced w/c value) - with the result of strongly decreasing rates of carbonation. One must also consider that the types of cement and the averidge strength class of concrete have changed and will change over time. Thus there will be a difference between how much is taken up today and how much will be taken up in 50 years from now [Lagerblad_2005]. This change is exemplarily demonstrated by the shift towards cements of higher strength in Germany in the last 20 years (Figure 6).
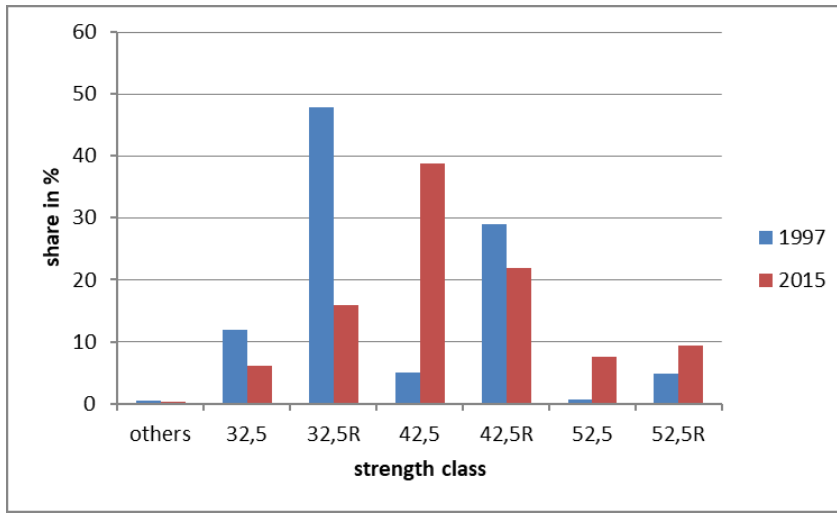
Fig. 6 Domestic shipping of cement of VDZ members by strength classes in Germany in 1997 and 2015 (VDZ_2016, Bundesverband der Deutschen Zementindustrie_1999)

It can be shown that domestic shipping of cements in Germany with strength classes equal to or higher than 42.5 raised from 39.5% in 1997 to 78% in 2015. This indicates an increased use of concrete with higher carbonation resistance.

5.2. Top-down approach – the macro perspective
5.2.1. Mortar structures

Two important questions will be critically examined below: Can the share of mortar in cement consumption be reliably estimated? Are the important parameters for the carbonation of mortar known or can they be reliably estimated?

The global market volume for mortars in the past and future is difficult to assess. Statistics are rare and inconsistent [Leopolder_2010]. For drymix mortars the global production volume is estimated to approximately 180 million t for 2011 [Leopolder_2010] and 200 million t by 2013 [Prabhakar_2013]. In this period, large annual growth rates were detected within emerging countries. Assuming an average cement content of 25% within mortars, a global demand of annual 50 million t of cement for dry mix mortar can be estimated. The share of drymix mortars on total global volume of mortars can be assessed to 6-7%. Delivery of mortar on job sites differs from country to country. For mature markets the consumption of cement produced in manual bags was used as an indicator for mortar production on job sites. In Germany for example bag cement has a share of 7% on total consumption. In developing countries however, the infrastructure is usually lacking to use ready-mixed concrete for concrete structures. In those countries the concrete structures are built up to a relatively high share with cement of bags. On a global scale, Leopolder roughly estimates that 15 to 18% of cement globally produced is used for mortar application in 2014. This is in good agreement with an own simple assessment which indicates that the mass-ratio of cement used for mortars (masonry mortar and plasters) and for concrete for a standard house build by bricks is approximately 0.15. It can be assumed that in the past mortars were more important than they are today. In a recent study by ETH Zürich mortars and plasters have a share of 24% of the cement use for downstream products in Europe in 2015 (Figure 7) [Favier et al_2018]. Xi et al. estimated that mortars had a share of approximately 30% on the total global cement consumption of cement within the period of 1930 – 2013 [Xi et al_2016]. The value appears to be quite high. It is likely that mortars were more important in the past than they are today. However,

it is also difficult to distinguish the consumption of cement-based mortar from the consumption of air-hardening mortar based on quicklime.
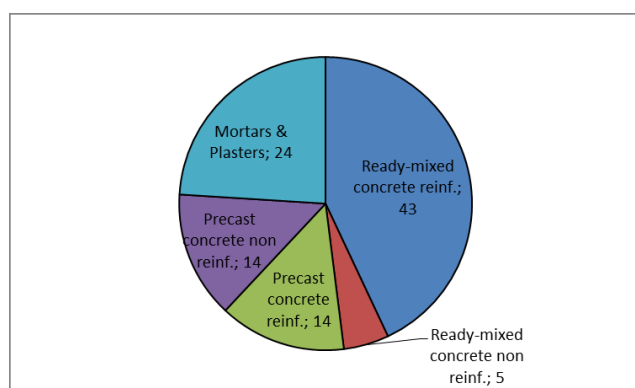

Fig. 7 Use of cement in applications in Europe in 2015 [Favier et al_2018]

There is consensus that direct air exposure of mortar structures leads to an accelerated carbonation due to relatively thin contact-layers. Whether this will generally lead to 100% carbonation within service life, is difficult to estimate but not unlikely for many cases. Common masonry mortar is mostly "shielded" by coatings, renders and plasters.

5.2.2. The existing building stock –the "sink"

Generell and Discussion of statements of IVL and Xi

Calculations of the actual CO_2-uptake rate of old concrete structures are associated with very large uncertainties. As mentioned, Xi et al. estimated that the cumulated amount of CO_2 sequestered globally in concrete structures (without mortar-based structures) during the period 1930-2013 equals an offset of 19% of the process CO_2-emissions released from the manufacturing of cement during the same period [Xi et al_2016]. This magnitude is also estimated in other studies balancing national stocks in European countries with regard to an uptake period of 100 years. The results are summarized in in a IVL-report [Stripple et al_2018]. As calculation base, an uptake of around 15-20% is suggested therein.

This estimation is based on the square root of time law. Regardless of whether this law is really applicable, specific information e.g. about the used cement types, quantities, w/c ratios, additives and admixtures for every year during the former 100 years of construction are necessary and have to be taken into account. The same applies to the future CO_2-uptake of buildings which are manufactured in the presence. With regard to concrete buildings, additional information about their exposure and surface to volume ratio as well as the presence of protective coatings and climate conditions are necessary. All this information is mostly totally lacking. In connection with uncertain models, simplifications and approximations the proposed results can only be of very limited accuracy.

In addition, it is proposed 'that the uptake during one year in existing buildings (stock) is equal to the uptake during (100) years in the concrete produced during the same year' [Stripple et al_2018]. This approach again presupposes an isotropy between historical, present and future concrete, which, as has been demonstrated within this article, does not exist in an arguable case. Stetic functions with regard to carbonation behavior are not applicable in any case in such time-horizons. As a consequence, such a highly simplified quantitative description does not establish a causal relationship between the

CO_2-uptake by the existing building stock and the projected future CO_2-uptake by the buildings constructed in the present year.

Further, it is presupposed for practical reasons, that the cement or rather concrete production remains almost constant for the construction period under consideration and the actual year [Stripple et al_ 2018]. This necessary assumption again highlights the fact that there is no direct link between future and present CO_2-uptake in the constructed environment. As global concrete consumption has risen massively over the last 20 years, such a presupposition does not exist for many regions such as China and India and is therefore not applicable for expressive calculations.

As just discussed, it is not legitimate to extrapolate the amounts of CO_2 sequestered by concrete in the past into the distant future. It is even less legitimate to offset current and future sequestration by buildings constructed in the past against the amounts of CO_2 released today or in the future by cement factories as published by Xi et al. [2016], since there is no link between today's emissions and the sequestration by historical products.

In other words, if no cement is produced in the year under consideration, already existing buildings would still absorb CO_2. The climate is fully burdened by the additional CO_2 released due to the production of new cement, not withstanding the fact that a small part of these emissions will be absorbed over the next 100 years.

The issue CO_2-absorption of the built environment touches also the question of allocation. Is it justified that today's cement industry claims the built environment (of the past hundred years) for itself, for whose construction they are mostly not responsible? From this perspective, balances in this respect are only justified if very short periods are considered, which keep the aspect of "originator" and thus responsibility manageable[2]. In addition, this approach minimizes the calculation uncertainties mentioned above. What is also needed is an integrated point of view. The CO_2-absorption should not be considered separately, but always in relation to CO_2-emissions in the period under consideration. The following model calculation demonstrates this aspect impressively[3].

Assuming all concrete structures constructed in one year would be walls of 25 cm thickness. This model would result in a surface per cubic meter of concrete of approximately 10 m², a rather high value in relation to real surface/volume ratios exposed to carbonation. Taking into account a relative high mean uptake of 20% of CO_2 during service life within a hundred years, a final carbonation depth of 26.5 mm on the average can be expected. The used mean k-value of 2.65 is relatively high (see table 1). This calculation suggests that in the first year of service life on the average 2% of the concrete would be carbonated. Therefore accordingly 2% of the Ca-content in clinker shipped and consumed in a specific region is carbonated in the first year.

Comparing the growth of CO_2-process emissions in the global cement industry in the last decades with the modelled CO_2-uptake of clinker in the first year of service life 1991-2016 shows that in most years in the period 1991 to 2016 this annual CO_2-uptake is even overcompensated by the growth in process CO_2-emissions (Figure 8). The sequestration of CO_2 is overrated in this context. For this comparison,

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[2] CemBR reports that 52 cement plants closed in the EU-region between 2005 and 2018. Who claims the building stock manufactured with the cement produced by these closed plants?

[3] We use one year as reference in this model. It could also be taken two or more years. We assume that with a well-processed concrete structure, the further growth of carbonation is nearly negligible after a few years.

we use data of Andrew [Andrew_2018]. If CO_2 from the thermal and electrical energy demand is added, only slightly more than 1% of the CO_2 emissions are sequestered within one year - 99% remain climatically effective.
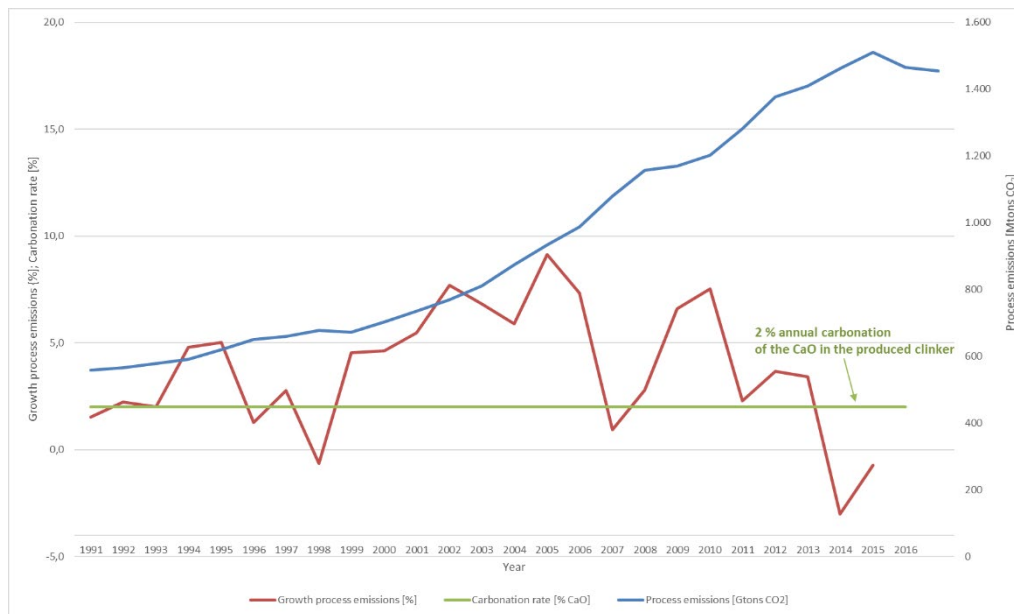

Fig. 8 Assumed CO_2-uptake of cement in the first year of service life versus the growth rate [in percent] of CO_2-process emissions in the global cement industry in the period 1991-2016. [according to data of Andrew_2018]

The term carbon sink

The use of the term *carbon sink* in the context of cement is not very happily chosen. Originally, within climate research terminology carbon sink is only used in the context of natural processes as stated for example by the global carbon budget [GCP_2018]. According to the European Environmental Agency (EEA) glossary [EEA_2019] carbon sink is defined as natural forests and other ecosystems that absorb carbon, thereby removing it from the atmosphere and offsetting CO_2-emissions". However the Kyoto Protocol allows certain human-induced sink activities undertaken since 1990 to be counted towards Annex I Parties' emission targets. An appropriate term would be *carbon sequestration* which the United Nations Framework Convention on Climate Change defines as the process of the removal of CO_2 from the atmosphere and depositing it in a reservoir [UNFCCC_2019]. The key point is that only a share of the theoretical possible amount of calcium within concrete will be carbonated during 100 years. Carbonation can therefore only adjust partly the CO_2-emissions of the cement industry. As consequence, conventional cement is a strong net CO_2-producer.

Long-term effect of sequestered CO_2 emissions

The final aspect discussed here seems of decisive importance: Every gram of CO_2 once emitted makes its contribution to the CO_2-concentration in the atmosphere. There are indications that equilibration processes with the ocean absorb most of the CO_2 released to atmosphere on a timescale of 2 to 20 centuries. A substantial fraction (20–35%) of CO_2 once emitted would remain in the atmosphere awaiting slower chemical reactions with $CaCO_3$ (neutralization to hydrogen carbonate) and igneous rocks. The remaining CO_2 is abundant enough to continue to have an impact on climate for thousands of years [Archer et al_2009]. Other studies come to the conclusion that the full effect of an emission may not be felt for several decades, if not centuries [Zickfeld_2015]. From this perspective, even if CO_2

is sequestered at a late stage – decelerated by a long-term delay, thawed tundra soil has not the possibility to capture methane back on; damages caused by extreme events cannot be retroactively reversed. From this perspective, it is actually relatively irrelevant for the sensitive climate system whether 10%, 20% or 40% of the CO_2-emissions caused by the cement industry are absorbed back into concrete within 100 years. There remain large net-emissions which have their strong contribution to the increase of CO_2-concentrations in the atmosphere.

6. Discussion of carbonation assessment after service life
6.1. General description after service life

The after service life is potentially the most important period of the life cycle of a concrete structure with regard to carbonation. Concrete is mostly crushed to varying grain sizes and either disposed of or reused as recycled construction material. By crushing, the reactive surface area is increased massively. In addition, permeability of individual broken pieces is increased by non-completed cracks. If the broken coarse fraction is used as aggregate in road construction, however, it is exposed to additional mechanical (e.g. driving, changes of frost and thawing periods) and chemical loads (e.g. de-icing salts, nitrate from agriculture, acid rain). Both the mechanical and the chemical attack may considerably accelerate the weathering.

6.2. Demolishing and recycling

After these general explanations it can be summarized that a CO_2-uptake can potentially take place when the concrete structures are demolished. Thus the fate of crushed concrete, the degree of fragmentation and the environmental conditions of the location where the crushed material is disposed of are of significant importance.

Andersson et al. analyzed the management systems at the recycling sites [Andersson et al_2013]. In Sweden the treatment can be divided into the following steps which can certainly be assumed as the common procedure:

1. Demolition of used concrete products.
2. Intermediate stockpiling of demolished concrete.
3. Crushing of demolition products resulting in a mixed size fraction. Steel rebar recycling.
4. Intermediate stockpiling of mixed crushed concrete fraction.
5. Use of the mixed concrete fraction in construction applications. Current examples are construction land filling, coarse road base or building foundations.

The crushed concrete mix can be assumed to be stored in piles with a height of several meters. Small size fractions are in principal subject of accelerated carbonation, but the stockpile has internal low air access. Carbonation can only be expected to a depth of a few centimeters. Andersson et al. assume approximately 2% carbonation in the piles [Andersson et al_2013].

However, even in this last phase of life, a distinction must be made according to the type of use. If the rubble is used in unbound road construction in underground applications, the internal access of air is again restricted. Therefore, carbonation is delayed or even prevented.

In total Andersson et al. expect that 11% of the maximum theoretical CO_2-uptake occurs today in the end-of-life period [Andersson et al_2013]. The question arises whether this figure is representative for the situation in a country in total.

There is a strong lack of information about the natural carbonation of demolished and crushed concrete [Lagerblad_2005]. Even the existing models for carbonation exclude that the concrete is crushed and recycled. Models of this stage have been performed by Pade_2007 and Andersson et al_2013. The problem of lacking information already applies to the issue service life, but has a completely different dimension for the after-service period.

One experiment of the CO_2-uptake in crushed concrete from a demolition site and recycling plant in Japan is reported by Kikuchia and Kuroda [20119. This study is several times quoted in literature due to otherwise missing data. Apparently, the authors performed only a few in situ measurements. The CO_2-uptake in 3 months summed up to 11 kg per ton of crushed concrete (ratio of particles with sizes up to 5mm about 24%! Maximum size: 40mm). This corresponds to 15% of the process emissions emitted decades earlier for the cement production in the crushed concrete if OPC is assumed for simplification. This is a remarkably high amount. There is no information about the past "history" of the investigated concrete. In summary, there is a lack of valid data even for rough estimates in this phase of life.

The EN 16757 suggests a CO_2-uptake in the end-of-life stage (demolishing, crushing, and storage) of 5 kg CO_2/m^3 of concrete with current treatment systems. With an average cement content of 330 kg/m^3 concrete, this corresponds to approximately 3% of the process emissions based on OPC [Stripple et al_2018]. The study of Xi et al. reports on the global scale an uptake in this stage of life to be around 1.5% of process emissions by crushed concrete and around 2.1% by mortar in debris [Xi et al_2016]. Thus, in total approximately 1.7% of the process emissions are sequestered in after service stage. All in all, the potential to increase this value by applying more advanced waste processing systems within this period is thought to be very large [Stripple et al_2018]. There seems theoretically the possibility of developing new procedures for crushed concrete which could increase CO_2-uptake manifold [Andersson et al_2013].

Concrete recycling generally protects natural resources and avoides the generation of waste. Unfortunately, the processing is often not economical as crushed concrete is a material with low value. The economic efficiency of recycling could be improved, if the sequestered CO_2 is allocated completely to the recycling activity. Under certain circumstances, even enhanced weathering could be possible. However, the framework conditions for implementation seem to us to be more difficult than generally assumed. Even if a separation of building rubble by type can be achieved on a large scale, grinding processes for the necessary increase in surface area are very expensive. In addition, large areas are required to allow unhindered access of air.

The complete allocation of sequestered CO_2 to the recycling product reflects the fact, that carbonation is a desired property of these products whereas the carbonation of concrete in construction is deleterious. As far as blast furnace slag or fly ash is concerned, the allocation to recycling would omit a reallocation of the (small) carbonation effect to the steel or coal based power industry.

6.3. Chemical weathering in addition to carbonation

The fine fraction from concrete crushing in building rubble reprocessing plants is usually applied as filling material or e.g. for the construction of noise barriers. Mechanical strength is lost by crushing, such that carbonation can advance rapidly and the material loses its buffer capacity. Other damage

mechanisms known from cement chemistry, such as nitrate attack (from agriculture) or ettringite or thaumasite expansion by sulphate-containing water may additionally accelerate destruction.

With an accordingly large surface area and reduced buffer capacity, also biological weathering by organisms settling on the concrete particles becomes important. Damaging of concrete drain pipes by sulphuric acid from microbiological activity is a phenomenon that has been known for a long time. The sulphuric acid results from the oxidation of hydrogen sulphide that is generated by the reduction of the sulphate contained in sewage. In case the crushed fine fraction is subject to weathering under reducing conditions, dissolved sulphate from the hardened cement paste is available for the microbial formation of hydrogen sulphide. In contact with the oxidising zone, sulphuric acid is released. To oxidize hydrogen sulphide, an about neutral pH value is required, which is reached rapidly by carbonation. Organic acids produced by some organisms completely decompose hardened cement paste. In this context, the increase of the organic content of concrete due to the use of organic additives is of relevance. It represents a potential source of nutrients. The influence of biota on weathering must also be taken into account. Weathering of hardened cement paste may be accelerated strongly by the growth of fungi on surfaces. Source and effects of other acids on carbonation and the mobilization of heavy metals are discussed in [Achternbosch et al_2003]

In summary, after service life concrete will be exposed to acids from natural (biological and microbial acidification) and man-made sources (nitrate from agriculture, acid rain). In Germany already pH values of about 4 are the rule in e.g. forest soils. These acidity will remove calcium and thus reduce the possible degree of carbonation. The magnitude of this effect is unclear. Furthermore, besides calcium other trace element e.g. heavy metals are also expected to be further mobilized. The immobilization of trace elements in intermediate phases occurring during slow weathering would be aggravated at least. This issue should not be neglected.

Finally, for environments that are not effected by agriculture and acid rain the spreading of old concrete causes an increase of the local pH of soils. This effect of basic industrial residues emitted into forest soils can be measured already: "The lowlands in northeast Germany are characterized by tendentially higher pH values that may not be attributed to the substrate." [Achternbosch et al_2003].

7. Summary and Conclusions
7.1. Is there a need to reconsider the climate impact of cement production?

Even though the hardened cement matrix is metastable and can be expected to be 100% carbonated in geogenic time scales, this finding does not change the effect of cement processing on climate. Carbon sequestration takes place over long periods of time with immediate effects of the emitted CO_2 on climate change. In addition there is no causal connection between cement processing in the past and in the future. Therefore a compensation of today's emissions with carbon that is sequestered by the existing building stock as calculated by Xi et al. [2016] ("net cement emissions") is unplausible.

7.2. Carbonation has a negative effect on concrete

As demonstrated in chapter 4 and 5.1, carbonation of concrete is well known and studied for a long time with regard to damage or defects of buildings by destruction from the surface. This effect is generally regarded as a *deterioration mechanism* for concrete structures. The recently expressed view of carbonation as a positive effect by some stakeholders seems politically induced and masks out the fact that carbonation lowers the pH in the cement matrix and therefore clearly increases steel corrosion in Reinforced-Concrete (RC)-structures [Ekolu_2016, Müller et al_2011]. As shown in figure

6, RC-structures have currently a share of almost 60% on the cement consumption in Europe. Therefore, carbonation is a potential risk for a high share of cement applications.

7.3. Assessment and correction of the estimations proposed by Lagerblad

A share of roughly 20% of the initial process CO_2-emissions is assumed to be absorbed during service life of concrete constructions within a hundred years by many models. This seems a rather high figure for structures meeting the standards - implying a mean end carbonation depth of about 25-30 mm. After 50 years of service life, further carbonation is likely to be negligible in the most cases [Lagerblad_2005]. The models based on the square root law assume an additional carbonation of roughly 40% in the period 50-100 years. At least for the conditions in Central Europe, a reabsorbed share of 10% of the initial process CO_2-emissions during service life is assumed to be a more realistic figure from the authors' point of view. In addition, the estimations from Lagerblad do not take new cement types and admixtures into account. The shifts towards cements of higher strength classes which can be clearly revealed from the cement statistics imply that concrete is currently more dense and shows a significantly lower propensity to carbonation as in the past. Concrete of class C35/45 may carbonize only a few millimeters during service life [Locher_2006] if appropriately processed in accordance to the standard.

7.4. The existing data base is not sufficient

No reliable correlation of carbonation and age

Contrary to the prevailing view, the wealth of data on real structures indicates that any general correlation between carbonation depth and age is difficult and associated with great uncertainties. One reason is that there is mostly no information from the past how these buildings were constructed and which construction materials and processes have been used. In addition, there are indications that damage cases are partly involved in the insitu-testing campaigns - cases that can be clearly classified as falling outside the standard.

Simple modelles are insufficient, the experimental database due to testing is doutful

To evaluate the carbonation rate and collect results in good time, accelerated tests in laboratory have to be used. The common model to predict carbonation depth is based on the diffusion law assuming that the carbonation rate is proportional to the square root of the time of exposure to CO_2. Undoubtedly, very elaborate and complex models have been developed. But the question remains whether the laboratory tests and models can be compared with natural processes. There is no general agreement on how to extrapolate from accelerated testing conditions to real performance.

Insitu-tests on real structures on the global scale are mainly based on the phenolphthalein test which is an indirect measurement of carbonation with doubtful results as criticized by many authors. In order to clarify this matter, completely different analytical methods must be introduced and used which are able to precisely determine the inorganic carbon in a certain layer. We suggest the determination of the total carbon (TC) and "inorganic carbon" (IC), supplemented by x-ray analysis. In this context, we also suggest that national research institutions could carry out large-scale measurement campaigns, possibly funded by appropriate funding agencies and ministries.

The next question to be asked is whether the used basics allow top-down models of total carbonation of structures in a constructed environment. Implementing Chinese data as in the study by Xi et al [Xi et al_2016] cannot be in all cases the general basis. Without further analysing the reported carbonation depths in China, it should be noted that the durability of concrete depends among others on the quality of the used cement. A report by the Deutsche Bank points out that low-quality cements were increasingly taken out of the Chinese market in the last years [Deutsche Bank_2014].

7.5. The after service life is of high importance

To the authors view, the existing studies concerning carbonation of concrete structures during service life may overestimate the effect (which of cause exists), whereas the potential in the period after service life is estimated at least theoretically as relatively high and as the more important.

After service life, concrete and mortars are crushed by demolition and processing. Due to the enlarged surface area, crushed concrete weathering is accelerated. The crushed concrete mix can be assumed to be stored in piles with a height of several meters. Carbonation can only be expected in thin layers. Further carbonation depends on the type of secondary usage.

Concrete recycling and enhanced weathering has the potential to significantly speed up the recarbonation. There seems theoretically the possibility of developing new procedures for crushed concrete which could increase the CO_2-uptake manifold [Andersson et al_2013]. The economic efficiency of recycling could be improved, if all the CO_2 sequestered during service life is completely allocated to recycling activities. New technologies as hardening by enhanced carbonation during concrete processing or recycling may change the situation. As business models for these technologies rely on CO_2-emission savings, there is a risc of double accounting if the assumed CO_2-uptake is already considered during cement or concrete production.

After service life, recarbonation will further proceed, accompanied by the risk of mobilization of trace elements, e.g. heavy metals. In the long term contaminations of the underground with trace elements can not be excluded. Barriers for pollution control would be needed.

7.6. Recommendation: No implementation of carbonation of concrete in global carbon balancing on the basis of current data

As a summary, the existing values (depth and k-factors) for carbonation are hardly provable as average figures for natural weathering. In this context, one must understand and confirm climate authorities, such as those from the Global Carbon Project, who are reluctant to include this issue in their global CO_2-budget balances. On the existing basis, the drafting of guidelines for IPCC appears to be very problematic. On the other hand, one must admit that climate researchers are generally struggling with uncertainties on the global level to estimate the absorption of CO_2 especially in natural sinks.

7.7. Political Assessment

The ongoing discussion on the sequestration of CO_2 by concrete is politically sensitive. The use of the term *carbon sink* in the context of cement carbonation is at least problematic. Originally, within climate research terminology carbon sink is only used in the context of natural processes as stated for example

by the global carbon budget [GCP_2018]. No matter how large the carbonation effects may be, whether at 10% or 20% for service life, cement production remains a strong net CO_2-producer.

In this context, the cement industry finds itself in a tricky situation. In the medium term, there is no alternative binder in sight that can substitute OPC in order to lower carbon emissions significantly [Achternbosch et al_2018, Dewald et al_2016, Favier et al_2018]. All that remains is CCS or the development of new low carbon binders. From the current perspective the realization conditions of CCS are unclear. There are serious indications, that the transition could be more difficult and much more delayed than expected [Achternbosch et al_2019]. For this reason, to the author's perspective, reinforced R&D in the field of radical innovations is strongly recommended. Knowledge generation will be a decisive competitive advantage in the future. Unfortunately structural and systemic barriers exist which have to be taken into account (Dewald et al_2016). Knowledge generation within the cement industry is frequently demand-driven. This is reflected in the customer-oriented organization of R&D in cement companys. Decentralized research operations might best address specific market needs. However, basic research might well suffer from this decentralization and user orientation. This mode of knowledge generation is reflected in structural patterns: even some of the largest global cement producers do not maintain centralized R&D facilities. The question arises whether the cement industry can master the challenges alone. To the author's point of view, a long-term cooperation of industry with national research centres for the development of alternative binders is an obvious option.

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