'CLAIMED CONCRETE CO$_2$ ABSORPTION INCORRECT'

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FRIDAY, FEBRUARY 10, 2017

ARTICLE

Nature Geoscience [1] recently stated that the CO$_2$ absorption by concrete during its lifespan is much higher than previously assumed. About half of the CO$_2$ emissions released during the calcination of the material is thought to be reabsorbed thanks to carbonation. A cement chemistry approach shows that this conclusion is not correct.

Based on the theory in various literature on cement chemistry [3-7], it appears that set cement can absorb a much lower amount of CO$_2$ than stated in the publication from Nature Geoscience [1, 2]. The publication in Nature Geoscience is so complex that it easily takes a reviewer a full working week to properly combine all the related studies. That is why we approach the carbonation of concrete (and cement) from a completely different angle. From this follows a realistic estimate that 1% of the CO$_2$ emitted during production can be re-bound by the concrete. Thus, considerably less than the aforementioned 50%.

An explanation.

CO$_2$ UPTAKE CHEMICALLY EXPLAINED

The carbonation of concrete is a chemical reaction in the cement in which carbon dioxide (CO$_2$) reacts with calcium hydroxide Ca(OH)$_2$ and forms calcium carbonate (CaCO$_3$) (for terminology see the 'Terminology' box):

Ca(OH)$_2$ + CO$_2$ + H$_2$O ==> CaCO$_3$ + 2H$_2$O

It is striking that water (H$_2$O) is also required for carbonation, about which more later.

A positive effect of carbonation is therefore that CO_2 is absorbed from the air. Incidentally, carbonation is generally seen as a problem. After all, it lowers the pH of the concrete, which may lead to the protection of the reinforcement against rusting no longer being guaranteed. But in this article, we only focus on the positive aspect, the CO_2 absorption.

EMISSION VERSUS ABSORPTION

CO_2 is released during the production of cement. This is partly due to the chemical reaction in the production of cement, and partly due to the energy required for production. Internationally, emissions fluctuate between 0.9 and 1.15 tonnes of CO_2 per tonne of cement (CEM I). Overall, you can say that the ratio of cement and CO_2 is about 1:1. Although the article in Nature Geoscience only calculates the CO_2 emissions as a result of the calcination, we think you should look at the total CO_2 output for making cement.

To determine what percentage of these emissions will be taken up again, an imaginary cement is calculated. To this end, the proportion of $Ca(OH)_2$ in that cement is first determined, because it determines the extent to which concrete carbonates.

QUANTITY OF AVAILABLE $Ca(OH)_2$ AND CAPTURED CO_2

$Ca(OH)_2$ is formed during the reaction of minerals from cement with water (hydration). The amount of minerals in the cement is therefore important. In this regard, we assume Portland cement (CEM I, see the box 'Portland cement versus blast furnace cement'). The mineralogical composition of cement, based partly on the time frame 1930 - 2013, is:

55% C_3S
15% C_2S
10% C_4AF
20% other minerals

The minerals C_3S and C_2S react with water to form $Ca(OH)_2$ (in addition to calcium silicate hydrates, or CSH). Compared to these cement minerals, this results in 40% and 18% respectively of $Ca(OH)_2$, calculated in mass [4]. The reaction of C_4AF with water also influences the amount of $Ca(OH)_2$. However, no $Ca(OH)_2$ is released in this process, but approximately 30% of the $Ca(OH)_2$ is incorporated into the mineral structure and thus extracted from the 'carbonation stock' $Ca(OH)_2$ [4].

In total, this amounts to the following amount of $Ca(OH)_2$:

55% C_3S	x 40% $Ca(OH)_2$ after hydration	= 22% in set cement
15% C_2S	x 18% $Ca(OH)_2$ after hydration =	3% in set cement
10% C_4AF	x −30% $Ca(OH)_2$ after hydration =	-3% in set cement
20% other minerals		
Total available $Ca(OH)_2$ for carbonation =		22% in set cement

Thus, with complete hydration of cement, 22% $Ca(OH)_2$ will be released. Because you can bind 1 mole of CO_2 with 1 mole of $Ca(OH)_2$ (see reaction mentioned earlier), and the molar

mass ratio between $Ca(OH)_2$ and CO_2 is 74:44 (59%), 59% of the CO_2 can therefore be bound out of the $Ca(OH)_2$. In total, this is therefore 22 x 59 = 13%.

Intermediate conclusion: if all the Portland cement (100%) hydrates, at best only 13% CO_2 will be captured from the approximately 100% emitted during production (based on CO_2 emissions versus mass of cement of 1:1).

MOISTURE FRONT

Carbonation only takes place in the presence of a small amount of water (<50%). Dry concrete does not carbonate because water is missing; wet concrete does not carbonate because CO_2 cannot penetrate the water-filled pores in that case.
So concrete can only carbonate at the moisture front, the dividing line between wet and dry in a cement pore.
Full carbonation of concrete (so that all 22% $Ca(OH)_2$ reacts) is therefore the result of frequent moisture front movements in the cement pores, by wetting or drying out the concrete surface (for a longer period). This repeated drying out and re-saturation with water can be seen as a repeated refreshment of the air (CO_2) in the pores.
Examples of such concrete surfaces are undersides of gallery slabs. With concrete surfaces that regularly get wet/rained on, the dry front never penetrates more than a few mm into the concrete. Indoors, concrete dries completely once, whereby a negligible amount of $Ca(OH)_2$ carbonates once.
Incidentally, with further carbonation of the concrete, the CSH matrix can also carbonate. This reaction only takes place in the outer shell of low-calcium cements such as blast furnace cement. In Portland cement, this form of carbonation never actually occurs [6].

LESS THAN 13%

Above it was indicated that cement can only take up 13% of the 100% CO_2 output that was emitted during production. In practice, this will be much lower. There are two reasons for this.

REASON 1: DEGREE OF HYDRATION
The calculated value of 13% assumes 100% hydration. Because concrete seldom has a higher water-cement factor than 0.55, concrete will seldom if ever have a higher degree of hydration than 60% for a Portland cement CEM I 32.5 and approximately 80% for a CEM I 42.5 [graph 4 of 7]. Because the research spans several decades (1930 - 2013), we assume a hydration rate of 60%. The 40% unhydrated cement cannot carbonate.
This means that of the aforementioned 13%, only 8% CO_2 is absorbed.

REASON 2: CARBONATION DEPTH
Concrete will never carbonate over the entire cross-section, even if it is in conditions favourable to carbonation.

Locher reported in [5]:

Maximum carbonation depth of concrete after (estimated) 30 years in an industrial environment protected against precipitation in Duisburg-Rheinhausen (Germany) is for a B15 to 30 mm and for a B45 to 3 mm carbonation depth.

Other authors and researchers also arrive at comparable predictions and test results.

This means that by no means will all of the concrete carbonate, even under these conditions favourable for carbonation.

We assume a carbonation depth of 20% of the concrete thickness. This corresponds, for example, to 30 mm carbonation depth with a wall thickness of 150 mm, or 120 mm carbonation depth with 600 mm wall thickness.

REASON 3: LOCATION OF CONCRETE

As mentioned, concrete does not carbonate under all circumstances, but especially when surfaces are 'protected outside'. Not all concrete surfaces are in those conditions. But because other surfaces also always show some carbonation, we make a loose estimate 50% of all the surface carbonates.

CONCLUSION

If we take these three effects together, so 60% average hydration (reason 1), 20% carbonation depth (reason 2) and 50% carbonatable surface (reason 3), at a maximum theoretical CO_2 bond of 13%, only about 0.8% of the total CO_2 output can be bound. That is significantly less than the 50% mentioned in [1 and 2].

MODERN CEMENT

In our example cement, we have assumed an estimated average mineralogical composition in the period 1930 - 2013. What about a modern cement?

A cement from ENCI Maastricht contains on average 63% C_3S, 13% C_2S and 9% C_4AF. For all cements (CEM I 32.5 to 52.5), the set cement will consist of 24.6% $Ca(OH)_2$ at 100% hydration. By using this 24.6% $Ca(OH)_2$, 14.6% of the CO_2 can be re-bound from the atmosphere.

Suppose further that the hydration is not 60% but 80% (reason 1) and reason 2 remains unchanged. Then at most 1.2% of the CO_2 released during production will be re-bound through the life of concrete.

CONCRETE NOT CO_2 NEGATIVE

As far as we are concerned, it is evident that cement can never absorb the amounts of CO_2 mentioned in [1] and [2], however you calculate it. We therefore do not expect CO_2-negative concrete.

PORTLAND CEMENT VERSUS BLAST FURNACE CEMENT

Blast furnace cement reacts just like Portland cement with water to form set cement. Because blast furnace cement only partly consists of Portland cement clinker,

CO_2 binding capacity will also be considerably less. In addition, globally viewed, blast furnace cement only comprises a few percent of all cement used, especially in view of the 1930 - 2013 period examined. For this reason, these cements are not mentioned further in this note.

LITERATURE

1. Zhu Liu e.a., Substantial global carbon uptake by cement carbonation,
Nature Geoscience 9, 880–883, 2016.
2. **Vermeulen, E.M.M., CO2-footprint beton veel lager dan gedacht**,
Cementonline.nl, November 2016.
3. Neville, A.M., Brooks, J.J., Properties of Concrete. Pearson Education Limited, 1963.
4. Czernin, W., Cement chemistry and physics for civil engineering. Chemical Publishing Company, 1962.
5. Locher, F.W., Cement, principles of production and use. Verlag Bau und Technik, 2006.
6. Rooij, M.R. de, Cementsteen. Aeneas Media, 2010.
7. **Hoe poreus is beton, *Betoniek* 6/3**. Aeneas Media, March 1983.

EDITOR'S NOTE

The editors of *Betoniek* have read this article and have doubts about the correctness of the content. Schippers and Schenk are of the opinion that the Nature Geoscience article with the conclusion regarding CO_2 absorption is wrong by a carbonation factor of 50 to 60. This is even though several technical committees have examined the article in Nature Geoscience and have concluded that, in general, it does not provide new information and insights. The methodology is largely in line with EN 16757 (Sustainability of construction work) and other publications.
This significant difference of opinion in particular raises questions.

Part of the objections to the article by Schippers and Schenk concern the estimate of the percentage of concrete that carbonates. In the step from 13% to 1%, Schippers and Schenk only use concrete in the use phase. Mortars and the recycling phase are disregarded. And mortars and the recycling phase account for a significant part of the CO2 uptake.

Furthermore, Schippers and Schenk relate the CO2 absorption of concrete to the total CO_2 emissions, i.e. as a result of both the calcination and the energy used in cement production (according to their estimate approximately 1 tonne CO_2 per tonne of cement). The Nature Geoscience article is based only on CO_2 emissions from calcination, which is about 50% of the total.

However, the editors believe that a discussion on this topic is valuable. That is why we believe that we should provide space for the insights of Schippers and Schenk. If you would like to respond to this article, please send an email to **betoniek@aeneas.nl** and **info@slimbreker.nl**.

The editors