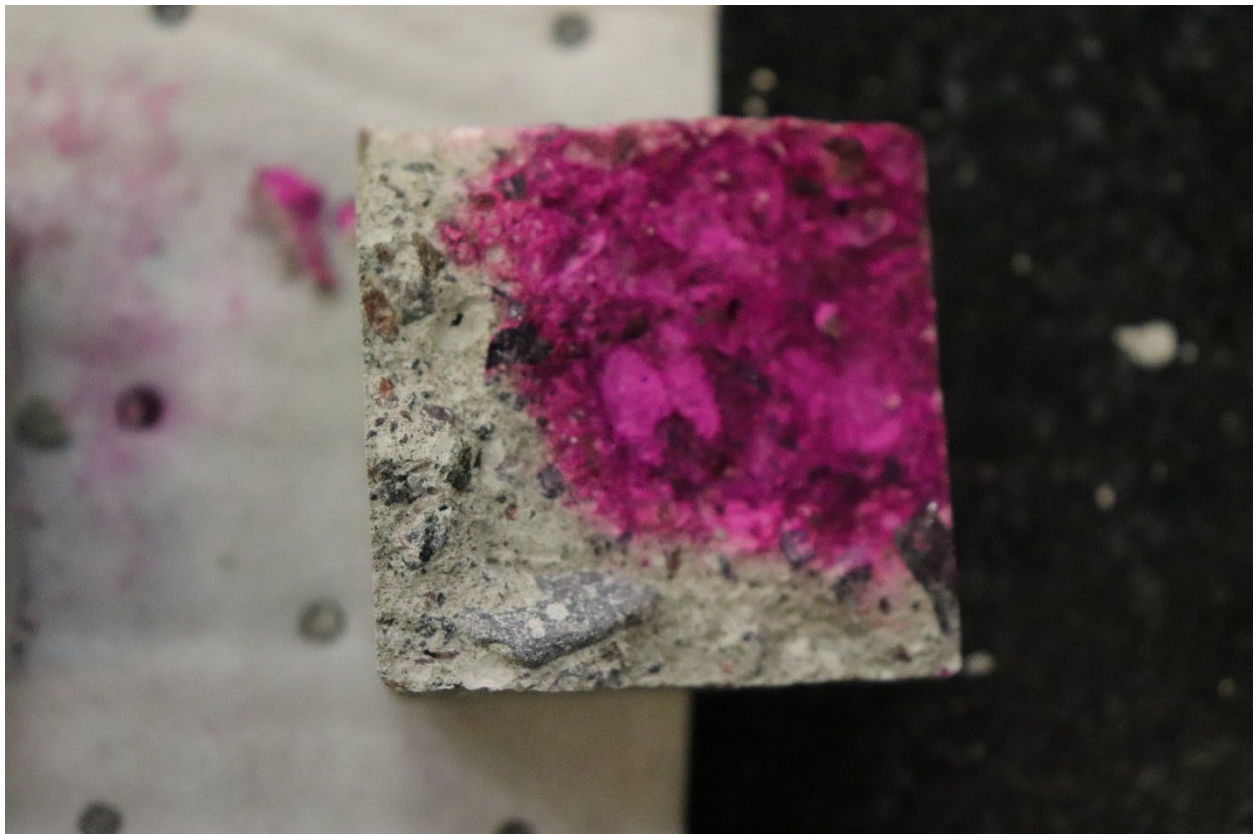


CUSTOMER REPORT

VTT-CR-00106-23



Final report: Carbonation of crushed concrete in field conditions

Authors: Tandr  Oey

Confidentiality: VTT Confidential

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beyond the obvious



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Summary It is of interest for CO ₂ capture to optimize carbonation of end-of-life concrete material during its disposal. The influence of fines removal and of weatherproofing were both studied for how they impact extent of carbonation in the field. It was found that to achieve optimal carbonation, fines should be removed or piles should be left exposed to the environment. In the case where fines are removed, it was found to be optimal to keep the pile covered such that it does not become saturated with water. Additionally, it was observed that the water-binder ratio of the concrete played a significant role in how fast carbonation proceeds, and that the carbonation observed likely depends on dissolved CO ₂ , particularly at and below disposal depths of 2 m. It is thus of importance for disposal of low water-binder ratio concretes to screen out fines, and for such a case to ensure the pile is unsaturated.	
Espoo, 31.1.2023	
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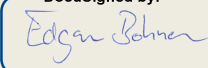


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1. Description and objectives

Concrete production accounts for approximately 8-10% of global carbon dioxide emissions. The majority of these emissions are due to cement production, specifically limestone de-carbonation, which is currently required for cement's core function as the binder component of concrete. This reaction can also proceed in reverse, and typically does over long periods of time at the concrete surface as the metastable cement hydrate phases re-carbonate to form limestone. While it is desirable to prevent this process from degrading the performance of in-service concrete, carbonation of otherwise unused demolition waste concrete represents an opportunity to re-capture some of these carbon emissions. The objective of the current project has been to identify what conditions can lead to optimal carbonation of concrete under field conditions. Specifically, the (1) size of crushed pieces and (2) moisture content of the deposited concrete due to weather conditions are both expected to play a role, because of how both control access of atmospheric carbon dioxide to the surface of the crushed concrete after it is deposited in piles. Secondly, the details of the concrete itself are expected to play some role (e.g., porosity, binder content, degree of hydration, etc.), and so two reference concrete mixes have been produced to undergo carbonation under this set of field conditions. Comparison of the extent of carbonation relative to these three factors will provide insight into the optimal field conditions for carbonation of concrete demolition waste, to maximize carbon dioxide re-capture.

2. Background and methods

2.1 Overview of factors influencing concrete carbonation

Carbonation of cement paste within concrete proceeds by a dissolution precipitation process, requiring the presence of at least some water. Carbonation results in multiple phase changes, but primarily results in the formation of calcium carbonate (calcite, Figure 1). Typically the calcium hydroxide phase (portlandite) carbonates first, followed by calcium-silicate-hydrate (CSH).¹

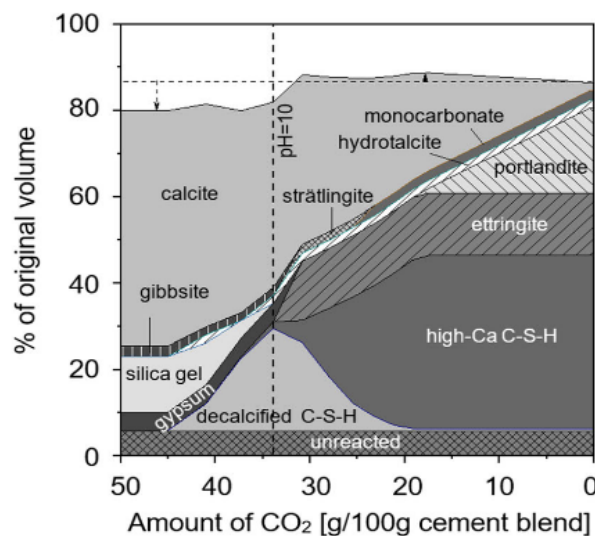


Figure 1. The thermodynamically modelled phase assemblage of a representative cement paste from Ref. [1], showing the sequential carbonation of portlandite and then calcium-silicate-hydrate (CSH). The left axis of the graph represents complete carbonation of available calcium within the cement paste, except for that required to stabilize any sulphates present as gypsum.



The maximum amount of carbon dioxide re-capture ranges from 40-50% of the weight of Portland cement,¹ and proportionally less for cements that have been mixed with supplementary cementing materials such as limestone and blast furnace slag (as used in this study). Although the progress of carbonation is typically assumed to depend primarily on the diffusion coefficient of CO₂, thus forming a linear relation to the square root of time according to Fick's first law of diffusion, in reality carbonation products can block pores and result in lower carbonation rate depending on the initial porosity and degree of hydration of the cement paste of the concrete.¹ For the conditions under study, such changes in carbonation rate are expected to be caused by (1) seasonal change in pile moisture content and temperature, and (2) differences in the pore structure of the concrete caused by, e.g., water-cement ratio, air entrainment, or supplementary cementing materials. Regarding the replacement of cement by blast furnace slag in the concretes used for this study, this is reported to reduce portlandite content and result in formation of less pore-blocking phases,¹ both of which favour higher rates of carbonation. Likewise, limestone inclusion in place of cement is also reported to result in a higher rate of carbonation due to the increase in effective water-binder ratio (and thus open porosity).¹ Between the two reference concretes used, it is thus expected that the rate of carbonation will primarily be limited by factors relating to mix design, i.e., water-binder ratio, and factors relating to seasonal moisture and temperature conditions. The maximum extent of carbonation will be limited by the cement content of the binder (70%), the calcium content of the blast furnace slag, and the overall binder content of the concrete.

2.2 Materials and methods for field study of reference concretes

The two reference concretes were chosen to represent two different air contents (entrained air), and two different water-cement ratios, as shown in Table 1. The cement type, mix design, and other basic properties are otherwise broadly similar (Table 1, Table 2). Notably, despite the higher air content, Reference Concrete A exhibits a lower rate of carbonation based on laboratory testing for effective CO₂ diffusion coefficient (Table 2). This provides an initial indication that open porosity (correlated to water-cement ratio) is the primary factor in dictating carbonation rate, rather than total air content, wherein entrained air does not have as strong an impact on carbonation.

Table 1. Mix design details of the two reference concretes used in this study

water-	Reference Concrete A	Reference Concrete B
Cast date	10.09.2007	06.09.2007
Cement type	CEM II/A-M(S-LL) 42,5 N	CEM II/A-M(S-LL) 42,5 N
Water content (kg/m ³)	406	321
Cement content* (kg/m ³)	170	185
Water-binder ratio (unitless)	0,419	0,576
Aggregate content (kg/m ³)	1715	1828
Aggregate < 0,125 mm (%)	2,90	4,91
Aggregate < 0,250 mm (%)	8,60	12,0
Aggregate < 4 mm (%)	46,4	49,4
Plasticizer (VB-Parmix, %)	1,25	-
Air entrainment (Ilma-Parmix, %)	0,030	0,020

*Cement content indicated here is the as-supplied CEM II/A-M(S-LL), wherein roughly 30% of the cement clinker is replaced with finely ground limestone and blast furnace slag.



Table 2. Basic properties of the two reference concretes used in this study

	Reference Concrete A	Reference Concrete B
Slump (mm)	130	100
Density (kg/m ³)	2321	2363
Fresh air content (%)	7,0	4,3
Specific surface area (mm ² /mm ³)	24	19
Spacing factor (unitless)	0,20	0,30
Compressive strength (MPa)	39,0 ± 1,3	35,5 ± 0,7
28 day average carbonation depth (mm)*	3,85	5,81
56 day average carbonation depth (mm)*	5,61	7,10
CO₂ diffusion coefficient (mm/d^{0,5})*	0,75	0,95

*Laboratory carbonation was carried out at 21° and 60% relative humidity in 1% CO₂ gas, with the CO₂ diffusion coefficient calculated according to Fick's first law (steady state).

Equal-sized cubes of each reference concrete were produced with a masonry saw. Sets of cubes from both concretes were retained in the laboratory under saturated conditions at 20°C to act as non-carbonated reference materials during final testing. Additional sets of cubes were placed in the field within four piles at depths of 0,25 m, 0,5 m, 1,0 m, and 2,0 m. Sensors to monitor temperature, relative humidity, and CO₂ concentration were placed at these same depths in each pile (EE872, E+E Elektronik GmbH). Each pile was two meters in total depth, above an asphalt base. The size fraction of crushed concrete and weatherproofing of each pile varied as shown in Table 3, to differentiate between the effect of fines removal and the effect of direct rain. Crushed concretes used for pile construction were provided by Ekopartner, and the piles were constructed on the 1st of September 2021. It should be noted that exposure conditions were identical for the first three months, with weatherproofing applied later on the 30th November 2021. The piles were disassembled starting 7th November 2022, and the reference concrete cubes were retrieved for analysis. A limited set of the cubes was assessed for carbonation depth, and the remainder of the cubes were each crushed, ground, and thoroughly homogenized prior to determination of the final extent of carbonation. Quantitative assessment of the extent of carbonation relative to the laboratory reference pieces was carried out using thermogravimetric analysis (STA 6000, Perkin Elmer) to distinguish the thermal decomposition of calcium hydroxide and calcium carbonate.

Table 3. Field exposure details for the four concrete piles studied

Pile Index #	Size Fraction	Weatherproofing*
1	20 – 45 mm	No
2	20 – 45 mm	Yes
3	0 – 45 mm	Yes
4	0 – 45 mm	No

*Weatherproofing consisted of covering the top of the pile from rain.

3. Results and discussion

Results are divided between the monitoring data acquired from temperature, moisture, and CO₂ sensors, and laboratory analysis of the retrieved reference concrete cubes. The former provides an indication of external factors that are expected to influence the rate of carbonation under field conditions to provide context for final assessments, while the latter quantitatively demonstrates the extent of carbonation achieved over a year of environmental exposure based on the varying concrete size fraction and weatherproofing. It should be noted that while this data is expected to also correlate well to ongoing carbonation year-to-year, longer-term testing would be required to quantitatively estimate the expected slowing in rate of carbonation over such longer timespans.

3.1 Monitoring of the concrete piles

Although no clear trend is seen in either pressure or relative humidity throughout the one year period of measurement (all sensors remain saturated at 100% RH), a clear trend is seen in the CO₂ concentration over time. As shown in Figure 1a, CO₂ concentration rises over the first three months at all depths of piles 1 and 2 to approach that of the reference sensor (in open air), demonstrating that removal of fines has a strong influence on accessibility of the concrete to atmospheric CO₂. By comparison in piles 3 and 4 the CO₂ concentration does not approach the reference even after several months (Figure 1b). Compared to the influence of screening fines out, weatherproofing the pile appears to have less effect on CO₂ concentration.

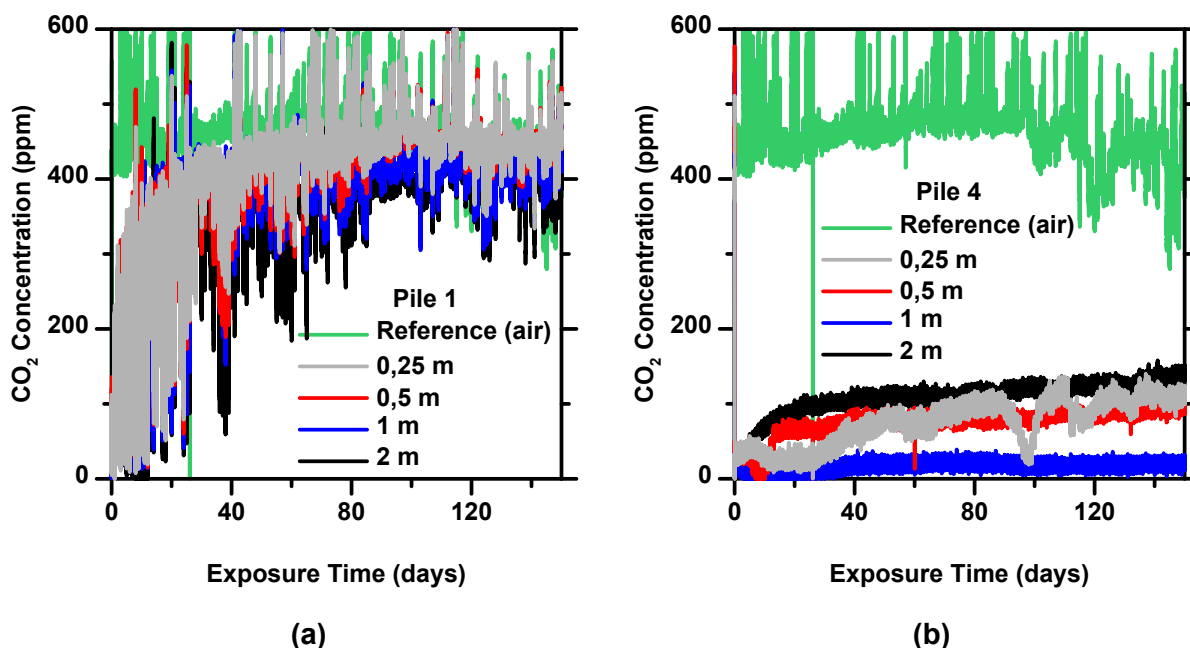


Figure 2. Representative illustrations of CO₂ concentration as a function of exposure time for (a) the piles screened for fines removal (Pile 1 is shown, though Pile 2 looks nearly identical), and (b) the piles made up of normal crushed concrete without fines removal (Pile 4 is shown).

Temperature in all piles shows the expected trend, following that of the reference sensor in air, and dropping below the freezing point of water between about 100 and 250 days of exposure (shown for pile 1 in Figure 2a). Following thawing, CO₂ concentrations are observed to remain stable, with a slight rise at the depth of 0.5 m (shown for pile 1 in Figure 2b). This is due to pile 2 being the only one that is not saturated with water (relative humidity is below 100%), and such a condition may favour carbonation preferentially at intermediate depth.

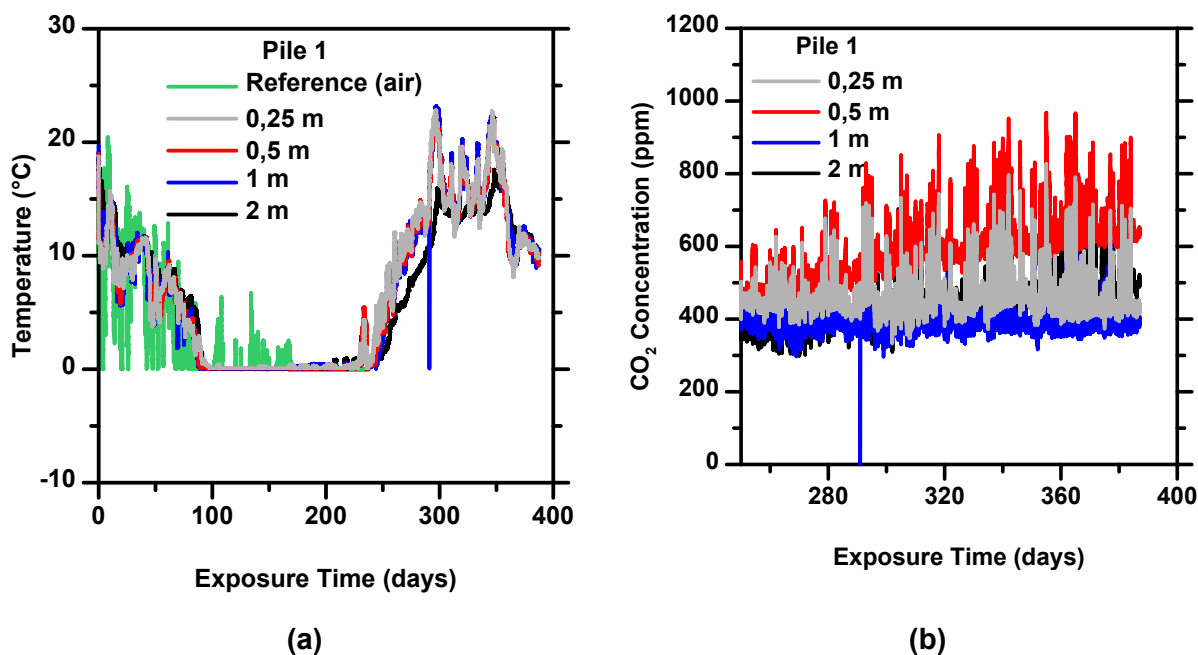


Figure 2. Representative illustrations of (a) the temperature along the depth of the pile, which broadly follows the seasonal variation measured by the reference sensor in air,* and (b) the CO₂ concentration over time following the rise in temperature back above the freezing point of water (after which point renewed carbonation is expected to occur).

*Due to freezing conditions, the reference sensor ceased to function along with many of the other sensors in February-March 2022. Only limited data, in particular for CO₂ concentration, is available after this point in time (mainly pile 1-2).

3.2 Characterization of reference concrete carbonation

Average carbonation depth across both concretes in all four piles (0,25 m depth) shows a clear trend of being higher in samples where fines were screened out (piles 1 and 2) and in samples present in the non-weatherproofed piles (2 and 4), as shown in Figure 3a. There is also a marked difference in carbonation of the two concretes, with concrete B experiencing up to three times as much carbonation due to its higher water-binder ratio (i.e., more open porosity). It is noteworthy that the carbonation fronts in the reference concrete cubes were only significantly on cast surfaces (as opposed to cut or fractured surfaces), as also expected due to the known higher porosity at such cast surfaces. Similarly to carbonation depth, the quantification of calcium carbonate by thermal analysis in the same set of samples shown in Figure 3b demonstrates the same trends: namely that removal of fines increases extent of carbonation, while weatherproofing reduces it.

The influence of sample depth on carbonation differs depending on if the pile is weatherproofed, with more carbonation occurring in the near-surface zone for exposed piles, but more occurring at depth in covered piles (Figure 4). This suggests that dissolved CO₂ also plays a significant role in carbonation, as also evidenced by the monitoring data (sensors were continuously submerged, indicating they only measured dissolved CO₂). Notably, the sample at a depth of 0,5 m showed higher than expected carbonation in pile 2, potentially supporting the late-stage monitoring data in piles 1 and 2 that indicated 0,5 m as the optimum depth for carbonation. It is likely that although the sensor was saturated with water, the full pile may not have been.

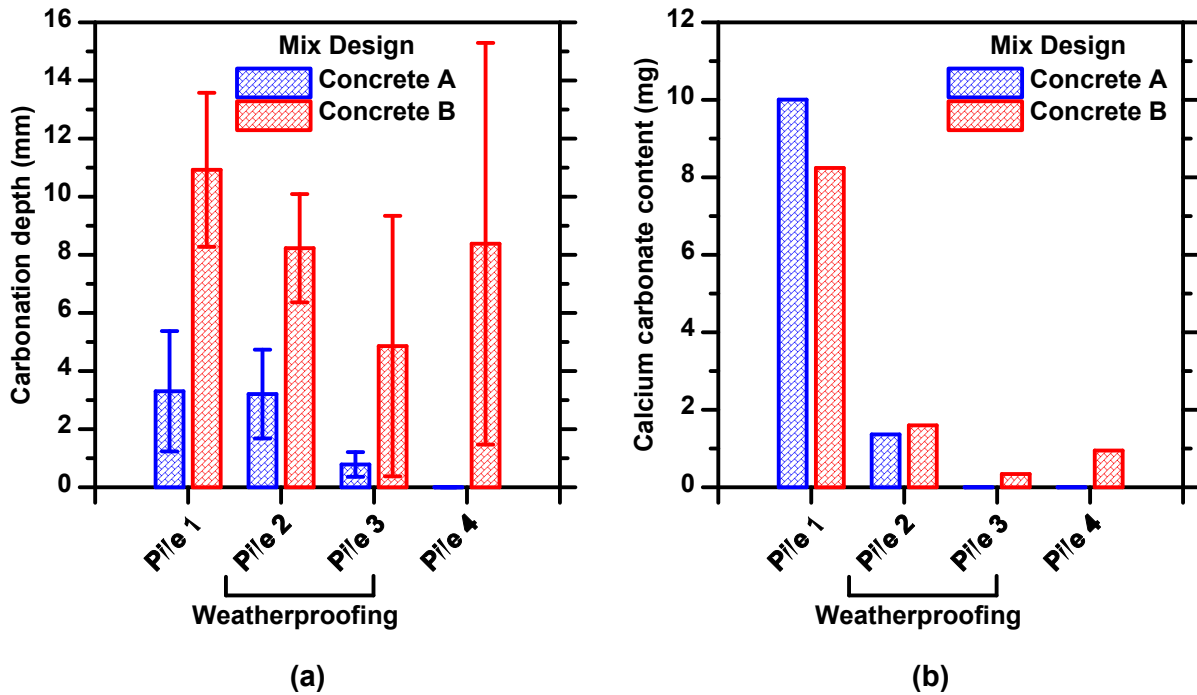


Figure 3. (a) Average carbonation depth measured for both concrete types from each pile at a depth of 0,25 m. (b) Calcium carbonate content (reference corrected to account for in-field carbonation) for both concrete types from each pile at a depth of 0,25 m.

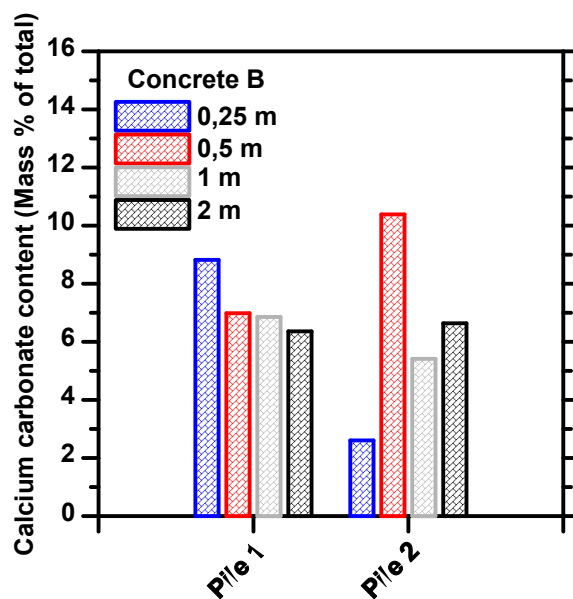


Figure 4. Extent of carbonation, expressed as mass percent of total sample, for thermal analysis determination of calcium carbonate across all depths for concrete B in pile 2.



4. Conclusions and summary

It was confirmed that optimal carbonation of end-of-life concrete can be achieved by removing the fines fraction from crushed concrete or by leaving the top of the concrete pile exposed. For the case where fines are removed however, it was found to be optimal to cover the pile, as the removal of fines appears to be required for the crushed concrete to benefit from the unsaturated conditions of relative humidity. This result is supported by all three data sources used: the monitoring data of CO₂ concentration, the carbonation depth assessments made on reference piece surfaces, and the quantitative analysis of calcium carbonate content of the same reference pieces. The most significant enhancements to carbonation appear to come from fines removal, and if possible from utilizing concrete with a high original water-to-binder ratio. Higher extent of air entrainment was shown to have little to no impact on increasing extent of carbonation, while weatherproofing of the piles was shown to moderately reduce the extent of carbonation generally, but in the specific case where fines were removed (pile 2) to result in optimum carbonation at a depth of approximately 0,5 m. This optimum depth may be site-specific and bears further study. Although weatherproofing significantly reduces near-surface carbonation, approaching a depth of 2 m equalizes carbonation between covered and uncovered piles, indicating that aqueous CO₂ plays a significant role in promoting carbonation in the field. It is likely that engineered systems to maintain a consistently high but unsaturated relative humidity would further optimize carbonation.

5. References

1. von Greve-Dierfeld, S. *et al.* Understanding the carbonation of concrete with supplementary cementitious materials: a critical review by RILEM TC 281-CCC. *Materials and structures* **53**, 136 (2020).

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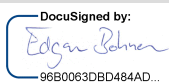
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