Challenge
Intentional carbonatization of cement and concrete is one step towards carbon neutrality of the building industry. Automated and reliable determination of CO_2 absorption rates is required for the product specifications of building materials

Solution
The multi EA 4000 C with automatic TIC module and FPG 48 allows fully automated TIC determination in solid building materials with automatic conversion to CO_2 contents

Intended audience
Manufacturers of building materials, esp. cement and concrete, recyclers of concrete

Determination of CO_2 Absorption Rates in Cement and Concrete Recycling by Automated Solids TIC Measurement

Introduction

Besides fossil fuel power generation and steel production, the cement and concrete industry is one of the heavy industries with the highest CO_2 emissions worldwide. More than 60% of CO_2 emissions are so-called process emissions, which are mainly released by the calcination and subsequent sintering of limestone. Another third of the CO_2 emissions is generated by the mostly fossil fuel that heats the rotary kilns to process temperatures of up to 1,500 °C.
In times of global climate change, it is necessary to reduce carbon dioxide emissions in all industrial sectors aiming for carbon neutrality. An increasing number of countries is striving towards the long-term goal of a "decarbonized society", i.e., a balance between emissions from anthropogenic sources and the removal of greenhouse gases by sinks.
In addition to replacing fossil fuels with more sustainable alternatives, such as substitute fuels or renewable fuels, the use of so-called carbon capture, utilization, and storage (CCUS) strategies is an eco-friendly option in the cement industry. Here, the CO_2 is first captured after combustion, using for example amine scrubbing solutions[1]. Extensive research is being conducted worldwide on the use of this captured CO_2. Among others, there is a method for the targeted carbonation of used concrete. The aim hereby is to increase the strength of concrete recyclates by reducing their porosity through binding of CO_2 in the material as calcium carbonate.
A fast, automated, and carbonate-specific measurement method is required to optimize the carbonation process and to detect the CO_2 absorption rate. In addition to X-ray diffractometry to determine the crystal phases in the hardened cement paste or differential thermogravimetry, the method of TIC (total inorganic carbon) determination according to DIN EN 15936[2] offers a very good possibility to determine the carbonation rate. In this standard the determination of the TIC is described as a partial

measurement of method A for the indirect determination of the TOC (total organic carbon) content. For this purpose, the finely ground sample (grain size < 250 µm) is weighed into a sample container, mixed with a non-oxidizing acid (e.g., phosphoric acid or hydrochloric acid). The resulting carbon dioxide is forced out by purging, stirring and/or heating, subsequently transferred to the detector (e.g., an NDIR detector) and quantified.

Materials and Methods

The determination of the parameter TIC was carried out by the multi EA 4000 C elemental analyzer with TIC solids module „automatic" and the automatic FPG 48 solid autosampler. A sample aliquot was weighed into a ceramic boat and was automatically acidified in the TIC reactor with 40% H_3PO_4. The CO_2 from the decomposed carbonate was released and directed to the NDIR detector via filters, drying agent, and a halogen trap. The carbon content in the measurement gas was quantified by NDIR (non-dispersive infrared) spectrometry. The calculation of the final result was performed automatically by the device's multiWin software.

Samples and reagents

- 7 cement and hardened cement paste samples, carbonated and non-carbonated
- Calcium carbonate for calibration
- 40% H_3PO_4 for sample acidifying
- Control mix A (TIC = 5% w/w) in accordance with DIN EN 15936: 44.13 g Na_2CO_3 + 18.83 g Na_4-EDTA x 4 H_2O + 37.04 g Al_2O_3

Sample preparation

All seven samples were fine, light greyish powders, that were weighed directly into the ceramic boats. A sample preparation was not needed.

Method settings

A standard TIC method from the device software library has been applied. The process parameters are given in Table 1 and 2. The general gas flow settings are 1.5 L/min (Ar/O_2) and 2.5 L/min (O_2) with an applied suction flow of 1.7 L/min.

Table 1: Process parameters for the automatic TIC determination in solids

Process parameters	
FPG parameter	TOC_IC/OC_inorganic
Amount of acid (TIC automatic)	800 µL
Furnace temperature	1,200 °C

Table 2: Detection parameters NDIR

Detector settings	
Max. integration time	300 s
Start	0.12 ppm
Threshold	3 ppm
Stability	3

Calibration

For this study, $CaCO_3$ (12% C) was applied as calibration material. Furthermore, diluted $CaCO_3$ (1 in 10 with Al_2O_3 to obtain a 1.2% C calibration standard) was used to create a lower calibration range. An independent 1.2% C standard and other reference materials were used for system testing. Calibration curves are shown in Figure 1 below. In Table 2 the calibration range is described.

Table 3: Calibration of the different parameters

Parameter	Standard	Content [% C absolute]	Weight [mg]	Calibrated Range [µg C]
TIC	$CaCO_3$ in Al_2O_3	1.2	16–163	190–1960
TIC	$CaCO_3$	12	12–51	1500–6000

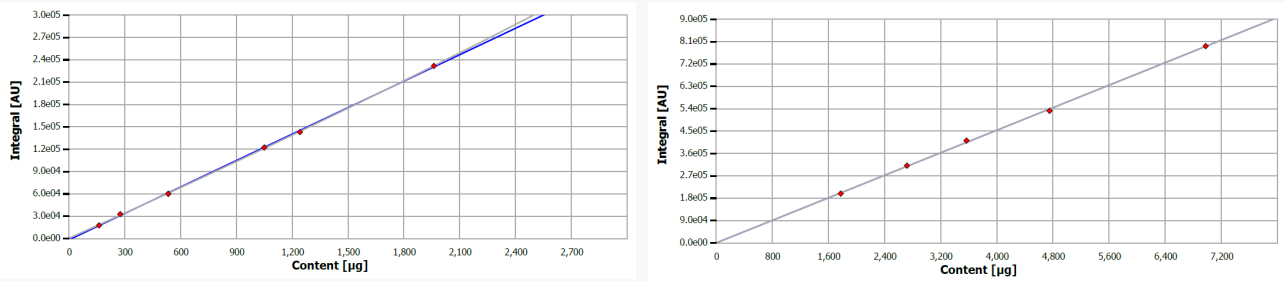

Figure 1: Calibration curves for the TIC determination, left: 1.2% C, right 12% C

Results and Discussion

The samples were measured as triplicates. Standard and reference materials were measured with two repetitions. Due to the limited availability of reference standards for TIC, a self-produced, diluted $CaCO_3$ (1.2% (w/w)) and control mixture A were used. The control mixture was prepared according to EN 15936 and had a TIC concentration of 5% (w/w). Measurement curves for the TIC determination are shown exemplarily in figure 2 - 8.

Table 4: Results of TIC / CO_2 determination

Sample ID	Sample weight [mg]	TIC ± SD (wt-%)	Equivalent to CO_2 [wt-%]
1 Cement paste, wet carbonated	45–53	7.68 ± 0.058	28.2
2 Cement paste, wet carbonated	44–54	7.30 ± 0.075	26.8
3 Cement paste, dry carbonated	43–53	6.08 ± 0.029	22.3
4 Cement paste, wet carbonated	47–53	7.03 ± 0.014	25.8
5 Cement, CEM I	46–56	0.42 ± 0.021	1.5
6 Cement paste, non-carbonated	50–54	0.89 ± 0.007	3.3
7 Cement, CEM I	48–59	0.57 ± 0.024	2.1
Diluted $CaCO_3$ (nom. conc. 1.2%)	49–70	1.22 ± 0.025	4.5
Control mix A (nom. conc. 5.0%)	47–53	5.06 ± 0.002	18.6

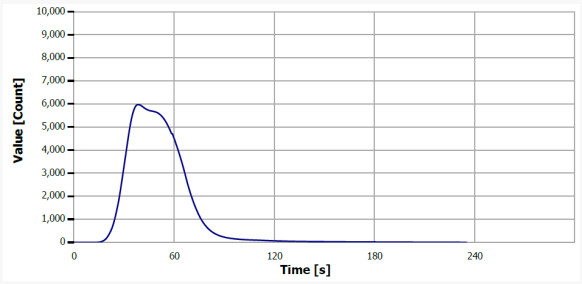

Figure 2: TIC measurement curve hardened cement paste 1, wet carbonated

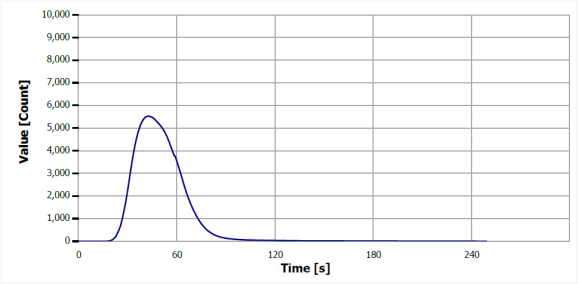

Figure 3: TIC measurement curve of hardened cement paste 2, wet carbonated

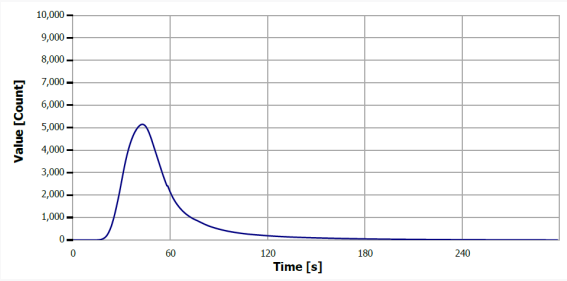

Figure 4: TIC measurement curve hardened cement paste, dry carbonated

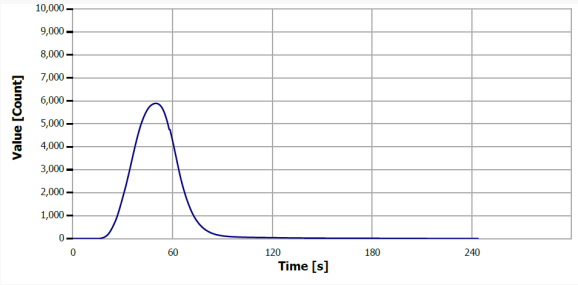

Figure 5: TIC measurement curve of cement paste 4, wet carbonated

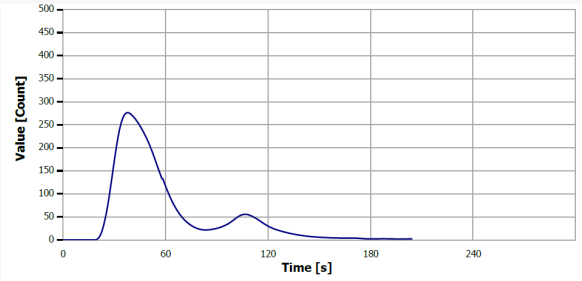

Figure 6: TIC measurement curve of cement, CEM I, 5

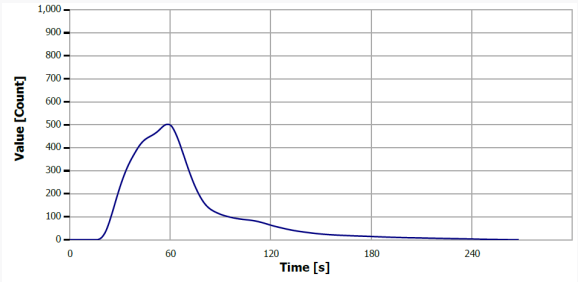

Figure 7: TIC measurement curve of hardened cement paste, non-carbonated, 6

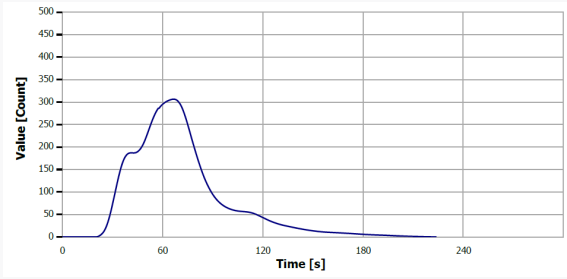

Figure 8: Measurement curve of cement CEM I, 7

Summary

The multi EA 4000 C is suited to analyze the provided samples for the determination of TIC. Automatic acidification works well and the reaction of the carbonates in the matrix is fast. The results are reproducible, and the standard deviations are low. With the short measurement times of max. 5 minutes and the 48 positions solid autosampler a high sample throughput can be realized while providing a high automation degree for the whole measurement process, including acid dosage. The used system configuration is shown in Table 5.
Other methods used for quantification of the carbonatization process in cement and cement paste samples are e.g., differential thermal analysis (DTA) / thermogravimetric analysis (TG) or also X-ray diffractometry examination of the carbonate phases in concrete samples. The degree of sample preparation, analysis time, or interferences to the results are much higher here. For example, for DTA the measurement time for a temperature range up to 1,000 °C is 1.5 hours at heating rates of 10 K/min. and besides decarbonatization also crystallization water interferences, resulting in loss of masses. Looking into these alternatives the automated TIC determination by the multi EA 4000 is most CO_2 specific and therefore the method of choice to determine carbonatization levels in cement and cement products.

Figure 9: multi EA 4000 C with TIC solids module „automatic“ and FPG 48

This configuration can also be used to directly measure the TC (total carbon) and the TOC in direct and difference mode. The multi EA 4000 can be further upgraded to automatically determine organically bound chlorine, as well as elemental carbon and total sulfur contents.

Recommended device configuration

Table 5: Overview of devices, accessories, and consumables

Article	Article number	Description
multi EA 4000 C	450-126.564	Elemental analyzer for the C determination
Solid autosampler FPG 48	450-126.574	For automatic sample feeding of solid or paste like samples (48 positions)
TIC solids module “automatic“	450-126.576	Module for automatic TIC determination

References

[1] Application Note: TIC Determination in Amine Scrubbing Solutions for Efficiency Control of CO2 Emission Reduction from Fossil Fuel Combustion

[2] DIN EN 15936:2022 Soil, waste, treated biowaste and sludge – Determination of total organic carbon (TOC) by dry combustion

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