

ACCELERATED CARBONATION TEST OF CONCRETE USING DYNAMIC GAS SORPTION AND MASS SPECTROMETRY

CONTEXT

Hardened cement paste (HCP) is the glue in concrete and mortar. HCP is a porous heterogeneous material composed of mainly Calcium Silicate Hydrates (C-S-H). These are of micron to nanometer size forming pores on a nanometer scale. Thus, HCP can be regarded as a colloidal system where surface forces play a remarkable role. Adsorbed water molecules interact with the surface. Capillary condensation occurs in the pores below bulk conditions acting in form of capillary and disjoining forces, latter can reach into GPa ranges. All these forces can alter the morphology and properties of the hardened cement paste depending on the moisture content. Pore size distributions were measured with BELPORE mercury intrusion porosimetry on hcp specimens, which had been prestored over the entire range of relative humidity [1].

Carbonation is an essential phenomenon impacting concrete durability and performance, especially considering CO₂ emissions and sustainability [2]. The CarbO₂crete project [3] developed a rapid and efficient method to record, quantify, and model the carbonation process in concrete materials. This application note overviews the innovative measurement setup, methodology, results using dynamic sorption (BELCAT II) coupled to mass spectrometry (BELMASS II).

Carbonation of concrete is a time-dependent reaction between CO₂ and hydrated cement phases, primarily converting calcium hydroxide to calcium carbonate. Traditionally, assessing this process and its long-term consequences requires lengthy exposures (month to years).

The aim of “AsmoM – CarbO₂crete” project was to establish an accelerated, quantifiable, and reproducible protocol that enables:

- Fast determination of carbonation rates and depths
- Modeling for long-term prediction under variable CO₂ concentrations and humidity
- Evaluation of concrete formulations and novel cements for CO₂ uptake capacity.

This application note will focus on the experimental setup.

MATERIALS AND METHODS

Concrete Samples:

Three types of synthesized cement samples (CEM I 42.5 R, CEM III/B 32.5 N, Ca(OH)₂ reference) were used (**Table 1**). Cubes (5–10mm) were stored under alkaline conditions to prevent atmospheric carbonation, then dried/crushed for testing.

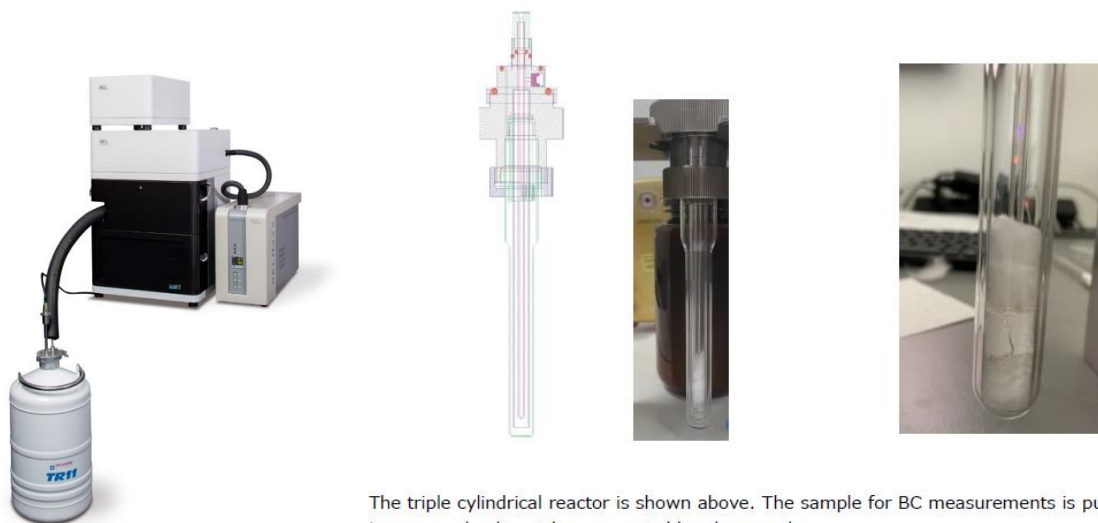
Table 1. Cement Sample Properties

Abbreviation	Cement Type	Strength (N/mm ² , 28 days)	w/c Ratio
CEM I	Portland	42.5–62.5	0.4
CEM III/B	Blastfurnace	32.5–52.5	0.4/0.5
Ca(OH) ₂	Reference	—	—

Measurement Setup:

A dynamic breakthrough curve approach was adopted using BELCAT II, coupled to BELMASS II Quadrupole Mass Spectrometer.

- Cement powder held between glass wool in quartz tubes
- Carrier gas: He, with programmable CO₂ (400 ppm to 10 vol%) and humidity (0–75% r.h.)
- Temperature controlled via BELCryo (down to 25°C)
- Inlet concentration and flow via MFCs (CO₂, H₂O)



The triple cylindrical reactor is shown above. The sample for BC measurements is put in the inner sample glass tube, supported by glass wool.

Figure 1: **Left:** Device setup of BELCAT II + BELMASS II + BELCryo II.
Right: Sample tube with cement powder.

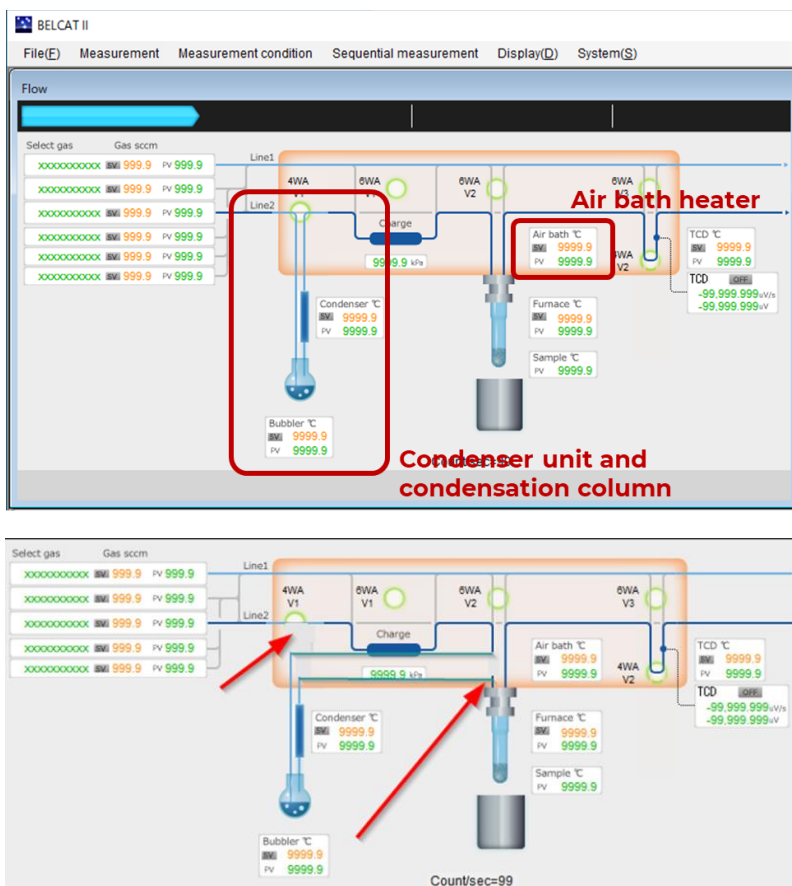


Figure 2: Scheme of BELCAT II for pulse humidification / standard configuration (**upper figure**) and continuous humidification / optional configuration (**lower figure**).

Humidification established with a unique two stage vapor generator for 100% saturation.

Experiment Workflow:

1. Equilibrate crushed cement sample with desired humidity oscillatory drying observed)
2. Sequentially pulse CO₂ at selected concentration
3. Monitor outlet gas composition with MS (m/z = 18, H₂O; m/z = 44, CO₂)

Calculate CO₂ uptake, analyze breakthrough curves.

RESULTS

Carbonation of cement-based materials

The carbonation process of cement-based materials is a chemical reaction of CO₂ with the pore solution Ca(OH)₂ forming calcium carbonate and water: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$

Pulse Humidification and Pulse Carbonation

Initial tests using synchronous pulses of water and CO₂ (**Figure 3**) showed:

- CO₂ rapidly penetrates pore system; breakthrough curve presents rapid rise.
- H₂O shows delayed breakthrough, with desorption controlled by sample moisture content and humidity.

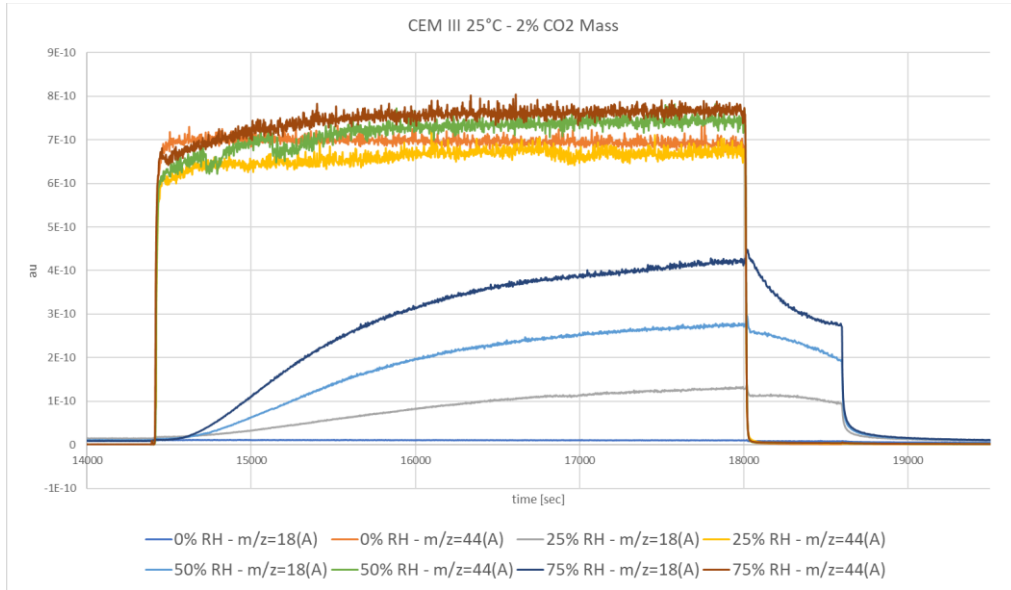


Figure 3: Example breakthrough curves, CEM III at 2 vol% CO₂, various r.h.

Continuous Humidification & Pulse Carbonation

Improved setup enabled continuous humidity flow, with CO₂ pulses. Key findings:

- Oscillating drying observed until moisture equilibrium is reached (Figures 4–5).
- CO₂ uptake and breakthrough curve shape strongly dependent on both w/c ratio and ambient relative humidity.
- At 50% & 75% r.h., equilibrium achieved more slowly; excessive humidity slows CO₂ diffusion (agrees with literature).
- Peaks of excess water are observed directly after CO₂ pulses (Figure 6). This amount of water is related to the carbonation process of the cementitious surfaces. Calcium carbonate crystals are formed quickly but will most probably decrease additionally further CO₂ diffusion into the hcp sample depth. This ongoing and slowed down carbonation process may also be a reason for an observed baseline shift of the water after CO₂ pulses. The amount of excess water is highest at 50% rh (Figure 7), corresponding to literature findings [2].

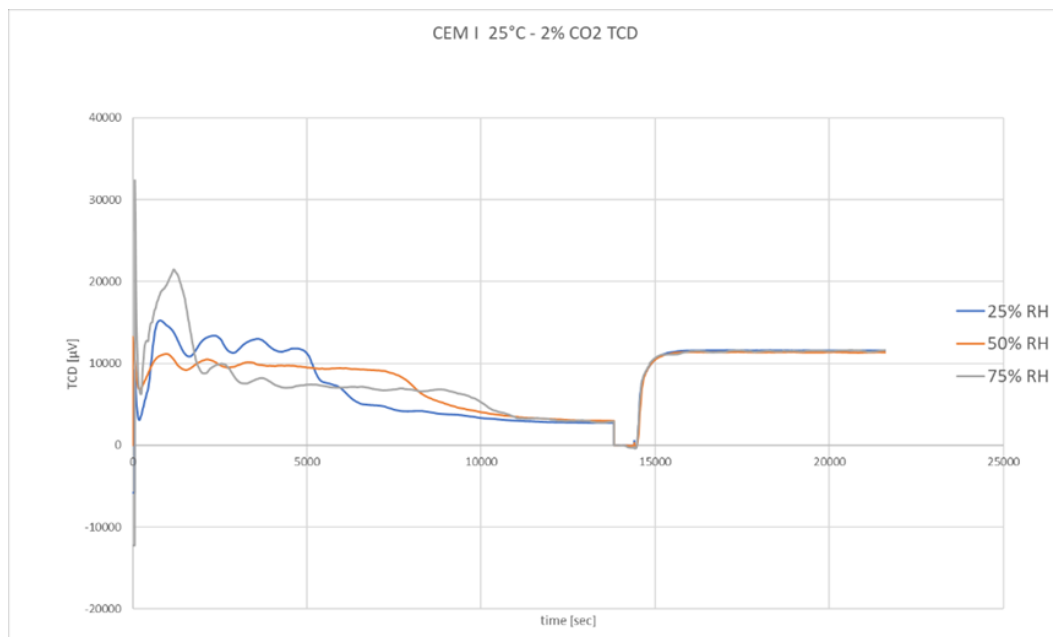


Figure 4: Oscillating H₂O drying behavior.

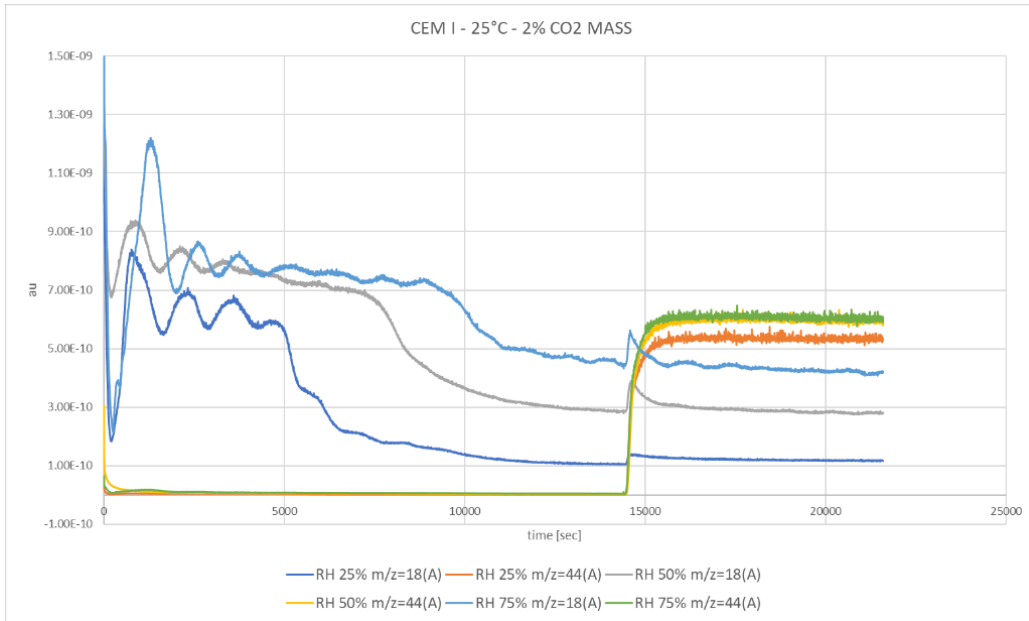


Figure 5: CO₂ breakthrough at different humidities, CEM I, w/c = 0.4.

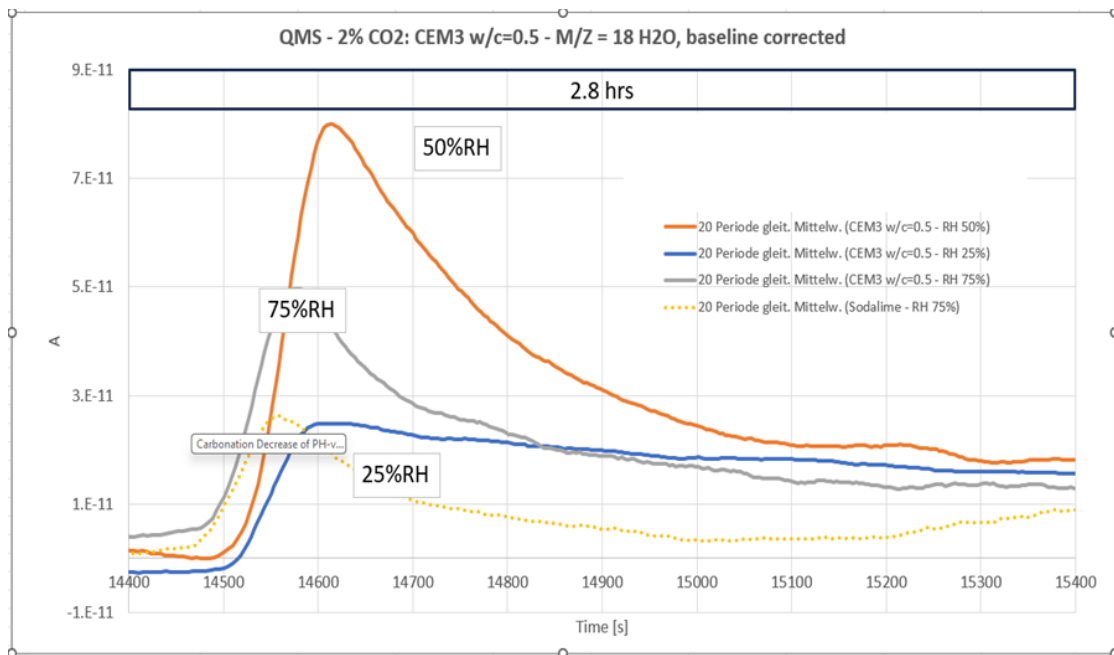


Figure 6: Water excess due to carbonation, enlarged from the peaks in Figure 5.

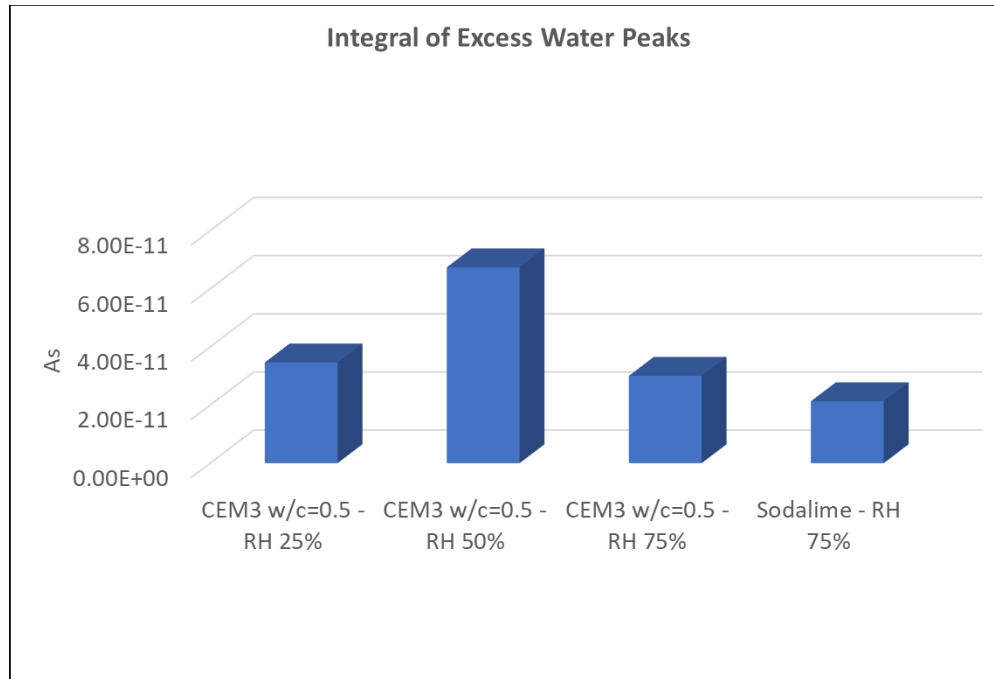


Figure 7: Integral of the water excess due to carbonation, with a maximum at 50% rh. This finding corresponds to findings in [2].

Additional Observations

- Blank runs confirm system stability and show no significant adsorption in the absence of samples.
- Variation of mass loading confirms proportionality for CO₂ uptake measurement.
- Soda lime (as standard) is used for reference validation.

CONCLUSION

- The developed method provides accelerated, reproducible, and quantitative assessment of carbonation in concrete within hours or days, compared to months/years with classic approaches.
- The approach supports material optimization, rapid benchmarking of new cements/concretes, and can be adapted for CO₂ capture or direct air capture sorbent testing.
- This new method provides rapid data for model-based extrapolation, enabling confident prediction of long-term durability and CO₂ resistance under real-world conditions

In conclusion, only a better understanding of the interactions between humidity and the hardened cement paste as a nanoporous, colloidal hydrate system will ultimately lead to a significantly greater durability of concrete structures in construction practice. Moreover, a more reliable, broadened knowledge of the interactions between water and cement paste on the micro and nano levels is of crucial importance for modeling, simulation, and life cycle forecasts.

BELCAT II & BELMASS II Breakthrough Curve carbonation analysis of hardened cement paste at various moistures stands for:

- Breakthrough Curve Analysis under real environmental conditions
- Fast and accurate measurements of carbonation on moist materials
- Advanced results for cement-based materials under real-life conditions

REFERENCES

1. Adolphs, J., Heine, P., Setzer, M.J.: „ Changes in Pore Structure and Mercury Contact Angle of Hardened Cement Paste Depending on Relative Humidity“, Materials and Structures Vol. 35, 477-486 (2002).
2. Adolphs, J. “Physico-Mechanical and Chemical Properties of Hardened Cement Paste Interacting with Moisture” invited keynote lecture paper RILEM Proceedings 5th International Essen Workshop - Transport in Concrete 11.-13. June 2007, pp. 181-194.
3. Adolphs, J. et al., BMfW ZIM Research Project 16KN090532, Final report “AsmoM-CarbO₂crete” 2024.

Discover the [Catalyst Characterization Analyzer BELCAT II](#)

