


Report of TC 238-SCM: hydration stoppage methods for phase assemblage studies of blended cements—results of a round robin test

Ruben Snellings  · Jacek Chwast · Özlem Cizer · Nele De Belie · Yuvaraj Dhandapani · Pawel Durdzinski · Jan Elsen · Johannes Haufe · Doug Hooton · Cédric Patapy · Manu Santhanam · Karen Scrivener · Didier Snoeck · Laurent Steger · Sui Tongbo · Anya Vollpracht · Frank Winnefeld · Barbara Lothenbach

Received: 29 June 2017 / Accepted: 1 August 2018 / Published online: 9 August 2018
© RILEM 2018

Abstract For many microstructural studies it is necessary to “stop” cement hydration—to remove free water. This paper describes the results of a round robin test on the impact of hydration stoppage methods on the composition of hydrated cements. A regular and a fly ash blended Portland cement hydrated for 90 days were selected. Ten laboratories participated in the round robin test. Four common hydration stoppage methods were studied: (1) oven drying at 105 °C, (2)

solvent exchange by isopropanol, (3) vacuum drying and (4) freeze drying. After the stoppage of hydration powder samples were studied by thermogravimetry (TG) and X-ray diffraction (XRD). Bound water and Ca(OH)₂ content were determined based on the TG data. Portlandite and ettringite content were quantified by Rietveld analysis of the XRD data. The goal was to establish interlaboratory reproducibility and to identify the best available protocols for research and standardization purposes. Based on the results of the round

This report has been prepared by a working group within RILEM TC 238-SCM. The report has been reviewed and approved by all members of the TC.

TC Membership:

Chair: Nele De Belie.

Secretary: Barbara Lothenbach.

TC Members: Natalia Alderete, Carmen Andrade, Susan A. Bernal, Laurie Buffo-Lacarrière, Jacek Chwast, Özlem Cizer, Luc Courard, Nele De Belie, Christos Dedeloudis, Emmanuel Denarié, Yuvaraj Dhandapani, Josée Duchesne, Pawel Durdzinski, Jan Elsen, Mette Geiker, Elke Gruyaert, Johannes Haufe, Duncan Herfort, Doug Hooton, Maria G. Juenger, Harald Justnes, Siham Kamali-Bernard, Agnieszka J. Klemm, Konstantin Kovler, Marina Kozhukhova, Barbara Lothenbach, José Fernando Martirena-Hernandez, Thomas Matschei, Esperanza Menéndez Méndez, Toyoharu Nawa, Van Tuan Nguyen, Angela Nunes, Cédric Patapy, John L. Provis, Jay Sanjayan, Manu Santhanam, Karen Scrivener, Kosmas K. Sideris, Ruben Snellings, Didier Snoeck, Marios Soutsos, Laurent Steger, Tongbo Sui, Yury Villagran Zaccardi, Jeanette Visser, Anya Vollpracht, Fengzhe Wang, Frank Winnefeld, Guang Ye, Monika Zervaki, Jian Zhou, Semion Zhutovsky.

Electronic supplementary material The online version of this article (<https://doi.org/10.1617/s11527-018-1237-5>) contains supplementary material, which is available to authorized users.

R. Snellings (✉)
Sustainable Materials Management, VITO, Boeretang
200, 2400 Mol, Belgium
e-mail: ruben.snellings@vito.be

J. Chwast · J. Elsen
Department of Earth and Environmental Sciences, KU
Leuven, Celestijnenlaan 200E, 3001 Leuven, Belgium

Ö. Cizer
Department of Civil Engineering, KU Leuven,
Kasteelpark Arenberg 44, 3001 Leuven, Belgium

N. De Belie · D. Snoeck
Magnet Laboratory for Concrete Research, Department of
Structural Engineering, Ghent University, Tech Lane
Ghent Science Park, Campus A, Technologiepark-
Zwijnaarde 904, 9052 Ghent, Belgium

robin test three recommendations are made. (1) Oven drying at 105 °C is not recommended. This dehydrates, alters and decomposes calcium aluminate hydrates significantly more than other methods and often produced carbonation artefacts. (2) Isopropanol exchange is the most appropriate hydration stoppage method for the study of the complete hydrate assemblage of cements, including calcium aluminate hydrates such as ettringite and AFm phases. (3) For quantification of portlandite ($\text{Ca}(\text{OH})_2$) all tested hydration stoppage protocols are satisfactory, with the exception of oven drying.

Keywords Supplementary cementitious materials · Hydration stoppage · Round robin test · Protocol · Blended cement · Hydration products

1 Introduction

Hydration stoppage is a practical necessity in the study of cement hydration. Stopping the hydration not only enables storing samples to analyse a range of material properties on the same sample at the same hydration age, it also makes the specimen less sensitive to carbonation, for instance during sample preparation before measurement. In addition, most material characterization techniques, e.g. thermogravimetric analysis, electron microscopy, Hg intrusion porosimetry, sorption experiments, etc. require dried samples to obtain reliable data.

Stopping the hydration of cement requires removing the free water in capillary pores available for the hydration reactions. At the same time, water contained

in smaller gel pores and as structural water in hydrates should not be removed to keep the cement microstructure intact and prevent the decomposition of the hydrate assemblage. Unfortunately, efficient removal of the free water alone is a difficult and practically impossible task and all effective hydration stoppage methods alter the hydrate assemblage to some extent [1]. However, it is well-recognised that there are large differences among hydration stoppage methods in terms of preserving the cement hydrate assemblage [1, 2].

Commonly used hydration stoppage methods either follow a direct drying approach in which liquid or solid water is directly removed from the sample by transforming it into vapor, or a solvent exchange approach in which free water is in a first step replaced by an organic solvent miscible with water and in a second step the solvent is removed by evaporation. The most commonly used direct drying techniques are oven drying, vacuum drying and freeze drying. Solvents commonly used for cement hydration stoppage are isopropanol, ethanol, methanol, acetone and diethylether. For each approach or method many different procedures are reported in the literature [2]. Given these differences it is not straightforward to decide upon which method preserves best the cement hydrate assemblage. Also, the robustness of the proposed methods is rarely established on an interlaboratory basis. It is therefore not clear if reported differences in microstructure or composition preservation are significant. It is not the purpose of this report to give an extensive overview of published work on the effect of hydration stoppage methods on cement hydrate assemblages. The reader is referred to earlier reviews on the topic [2–5]. Instead this

Y. Dhandapani · M. Santhanam
Department of Civil Engineering, IIT Madras,
Chennai 600 036, India

P. Durdzinski · K. Scrivener
Institute of Materials, EPFL, Station 12, 1015 Lausanne,
Switzerland

J. Haufe · A. Vollpracht
Institute for Building Materials Research, RWTH Aachen
University, Schinkelstrasse 3, 52062 Aachen, Germany

D. Hooton
Department of Civil Engineering, University of Toronto,
35 St. George Street, Toronto, ON M5S1A4, Canada

C. Patapy · L. Steger
Laboratoire Matériaux et Durabilité des Constructions,
INSA Toulouse, Avenue de Rangueil 135,
31077 Toulouse Cedex 4, France

S. Tongbo
Sinoma Research Institute, 16 Wangjing North Road,
Chaoyang District, Beijing 100102, China

F. Winnefeld · B. Lothenbach
Laboratory for Concrete and Construction Chemistry,
Empa, Swiss Federal Laboratories for Materials Science
and Technology, Ueberlandstrasse 129, 8600 Dübendorf,
Switzerland



contribution intends to assess the interlaboratory reproducibility of 4 commonly used hydration stoppage methods, using procedures established in consensus among 10 laboratories well versed in the study of cement hydration. The established procedures originate from a wide body of published research and in house experience and aspire to reflect the current best laboratory practice in the participating laboratories. It is tedious and outside the scope of this contribution to trace back the first reports of the key steps of the protocols, therefore only the main precursor documents are referred to here, without imparting claims regards to originality of such documents [1, 2, 5–8]. Further, this contribution aims to identify problems, including artefacts, associated with the methods when used to measure the representative hydrate assemblage characteristics of bound water, calcium hydroxide content, and ettringite content.

2 Participants and round robin test procedure

10 laboratories from 7 different countries participated in the round robin test. The materials, mix design, mixing and curing protocols, hydration stoppage protocols and material analysis protocols went through three rounds of internal discussion and amendments. Within the technical committee, presentation and discussion of the results took place only after delivery of all data and without revealing the origin of the individual data to the participants. Table S1 summarizes the participant contributions.

The work flow scheme of the round robin test is shown in Fig. 1. Materials were distributed as dry powders by VITO as coordinating laboratory. The

participants carried out mixing and curing of the cement pastes according to a fixed procedure. Subsequent hydration stoppage and material characterization was done by the participants. Each participant was requested to contribute data for at least 2 hydration stoppage methods and to report both raw measurement data and the analysis results. The analysis results were bound water content and $\text{Ca}(\text{OH})_2$ content as measured by TGA, and portlandite and ettringite content as measured by XRD analysed by the Rietveld method. In total there were 60 independent hydration stoppage experiments not including intralaboratory repetitions.

3 Materials

A commercial Portland cement (type CEM I 52.5 N) and a Class F (ASTM C618) coal combustion fly ash were used as starting materials. The chemical and phase composition of the starting materials is given in Table 1. The chemical composition was measured by XRF, and the phase composition was determined by XRD-Rietveld analysis using the external standard approach as described in [9]. The reported analyses in Table 1 were carried out by VITO as coordinating laboratory.

Two paste formulations were used in this study. The first sample was a pure Portland cement paste, the second a paste of Portland cement and fly ash, blended at a 70:30 mass ratio. The powders were mixed with deionized water at a 0.4 water to solids ratio (80 g solids + 32 g water) using an overhead laboratory mixer at 1600 rpm for 2 min. The pastes were cast in cylindrical (diameter 30 mm) hard plastic containers and seal-cured for 90 days at 20 ± 2 °C.

Fig. 1 Round robin test work flow. Materials are depicted in ovals, techniques and processes by rectangles

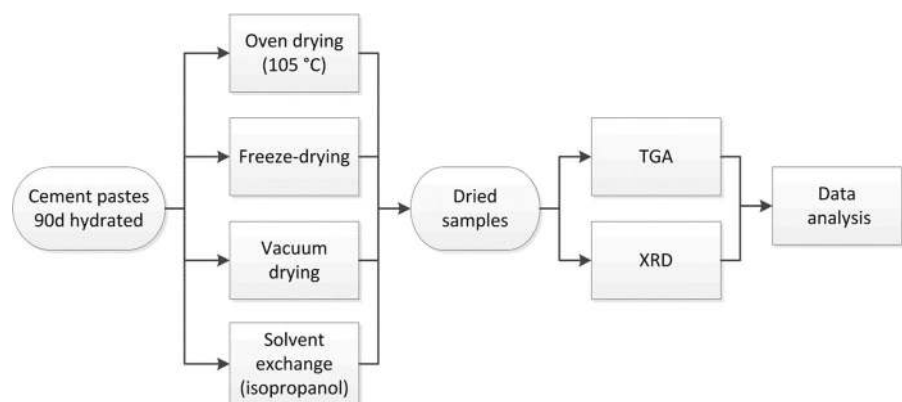


Table 1 Chemical and phase composition of the unreacted Portland cement (PC) and fly ash (FA) samples used in this study

XRF (wt%)	PC	FA	XRD (wt%)	PC	FA
Al ₂ O ₃	4.92	24.1	C ₃ S M3	64.9	–
SiO ₂	20.08	69.8	B-C ₂ S	10.3	–
CaO	64.27	0.1	C ₃ A orth.	8.7	–
Na ₂ O	0.31	0.1	C ₄ AF	7.9	–
K ₂ O	0.5	0.6	Quartz	0.3	12.5
MgO	1.83	0.2	Calcite	1.6	–
Fe ₂ O ₃	3.18	2.2	Portlandite	0.6	–
SO ₃	3.09	–	Anhydrite	3.7	–
TiO ₂	–	1.5	Gypsum	1.5	–
P ₂ O ₅	0.4	0.1	Mullite	–	16.2
Mn ₂ O ₃	–	0.1	Amorphous	0.5	71.3
LOI	1.5	1.4			
Sum	100.0	100.1			

At 90 days of hydration the hardened paste discs were prepared for sampling, 2–3 mm of edges were clipped and the top and bottom surfaces were gently polished to remove material that may have slightly carbonated. For each hydration stoppage experiment about 3 g of paste was sampled. The samples were crushed using mortar and pestle to below 1 mm, the 125 µm–1 mm fraction was retained for hydration stoppage. To rule out variation induced by sample preparation and storage, it was requested that optional duplicate samples for the hydration stoppage experiments were taken from the same hardened cement samples. 7 out of 10 participants reported duplicate results (Table S1).

4 Methods

Four commonly used hydration stoppage methods were included in this round robin: solvent exchange, vacuum drying, freeze drying and oven drying. The protocols were prepared in consensus, based on the expertise of the participants and represent commonly used methods for hydration stoppage. An overview of the protocols is given below.

4.1 Solvent exchange

3 g of crushed sample was immersed in 100 mL of isopropanol (technical grade) for 15 min. This is largely sufficient to exchange the isopropanol with the free water in the crushed sample and stop the hydration [1], and is in clear contrast to protocols where the samples are left up to 7 days or longer in the solvent which clearly affects the hydrates [10]. The suspension was vacuum filtered, rinsed once with isopropanol and twice with diethyl ether. The residue was dried for 8 min in a ventilated oven at 40 °C. Finally the dried powders were stored in a low vacuum (approx. 10 mbar) desiccator over silica gel until analysis. The solvent exchange protocol was carried out by all 10 laboratories participating in the test.

4.2 Vacuum drying

Immediately after crushing the crushed samples were transferred to a vacuum drying system operated at low temperature (– 78 °C) and low pressure (< 0.3 Pa). The samples were kept under vacuum for 7 days, having reached constant weight, and subsequently transferred to a low vacuum desiccator over silica gel for storage. Vacuum drying was carried out by 4 participating laboratories.

4.3 Freeze drying

The crushed samples were immersed in liquid nitrogen for 5 min before drying through sublimation in a freeze dryer operating at low temperature (– 78 °C) and pressure (< 0.3 Pa). The samples were kept in the freeze dryer for 7 days, having reached constant weight, and stored over silica gel in a low vacuum desiccator until analysis. 7 laboratories carried out hydration stoppage by freeze drying.

4.4 Oven drying

The crushed samples were placed in a ventilated oven at 105 °C for 24 h, having reached constant weight. The dried samples were stored over silica gel in a low vacuum desiccator until analysis. Oven drying was used by 9 participating laboratories.



4.5 Material characterization and analysis

TG and XRD measurements were made on all hydration stopped samples; before analysis the samples were finely ground using a mortar and pestle. The participants were asked to carry out the measurements as soon as possible after the hydration stoppage, if possible the same day, otherwise the samples were stored not longer than 7 days until analysis as described earlier [1]. Measurements were carried out one-by-one, avoiding carbonation in automatic sample changers.

The weight loss as a function of temperature recorded in the TG curves was measured over a temperature range of 30–1000 °C at a heating rate of 10 °C/min. A range of commercially available instruments was used by the participants. All participants except one used a sample mass of 50 mg, the one exception used a 100 mg sample mass. Nitrogen gas was stipulated as protective gas at a flow rate of 50 mL/min. The TG data were analysed to obtain following values: (1) Ca(OH)₂ content, (2) bound water content. The Ca(OH)₂ content was calculated using the tangential approach (integral) as illustrated in [11]. The bound water content was calculated using a stepwise approach, an integration over the temperature interval 40–650 °C was used, results were normalized to 100 g of anhydrous binder.

XRD measurements of the dried powders were made over an angular range of (at least) 5°–70° 2θ (CuKα). The maximum angular step size was set at 0.04° 2θ with a minimum integrated time per step of 2 s. The participants were advised to back or side-load the powders into the XRD sample holders to minimize preferred orientation effects. The recorded XRD data were used for quantitative phase analysis by the Rietveld method. The analysis results to be reported were: (1) the portlandite content and (2) the ettringite content, both normalised to 100 g of anhydrous binder. These phases were selected because they are relatively easy to quantify based on XRD data. All participants used their own XRD equipment and Rietveld analysis software (Table S2 in online appendix), however all participants did follow a consistent Rietveld quantification procedure. In this procedure, first a Rietveld analysis of the starting materials was made (the anhydrous Portland cement and the fly ash). The refined lattice and peak shape parameters of the crystalline phases in the starting

materials were copied and kept fixed in the Rietveld analysis of the hydrated samples. To rule out variation caused by the use of different starting crystal structures, a set of crystal structures was preselected and distributed among the participants, as in [9]. During refinement only scale factors, lattice and peak shape parameters were allowed to be fitted. Preferred orientation corrections were of the March–Dollase type and used sparingly. The presence of amorphous phase was taken into account by using a standard, both internal and external standard addition approaches were used by the participants.

5 Results

5.1 Raw TG and XRD data comparison

All participants were requested to supply the collected raw TG and XRD data. The intra- and interlaboratory comparison of the raw data proved to be very valuable in tracing back causes of variation in the final delivered data analysis results.

As a starting point of the comparison of the hydration stoppage methods, first characteristic differences are reported based on reproducible trends in the raw data. Figure 2 shows the TG curves, of the two hydrated cements treated according to the four hydration stoppage protocols. Only data reported by one

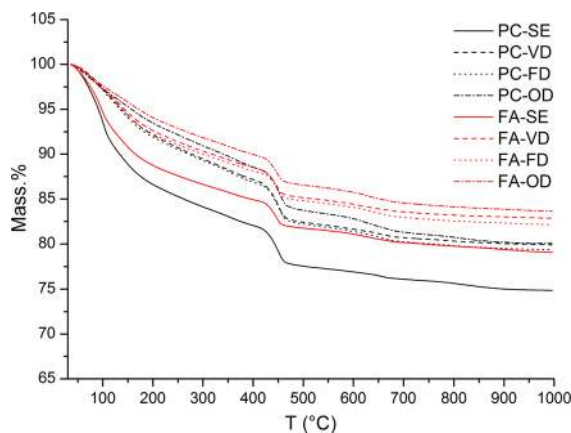


Fig. 2 Comparison of the TGA results amongst different hydration stoppage methods for 1 participating laboratory (EPFL). The results for both the reference Portland cement (PC) in black and the fly ash blended cement (FA) in red are shown. *SE* solvent exchange, *VD* vacuum dried, *FD* freeze-dried, *OD* oven dried at 105 °C. (Color figure online)

participating laboratory are shown for clarity. The overall trends and differences in raw data amongst the hydration stoppage methods are representative for the data supplied by all participants. Following trends were consistently observed for both the Portland cement and the fly ash blended cement.

The mass loss over the 40–300 °C temperature interval was highest for the solvent-exchanged samples. The mass loss of the vacuum and freeze-dried samples were very close and intermediate to the solvent exchanged (highest mass loss) and the oven dried samples (lowest mass loss). Clearly, the direct drying techniques removed significantly more water from hydrate phases such as C–S–H, ettringite and AFm as also demonstrated in [11].

The weight loss over the portlandite dehydroxylation interval (400–500 °C) was very similar for all hydration stoppage methods and for each hydrated sample. This is clearly shown in the DTG signals in Fig. 3.

Weight loss related to carbonation (600–800 °C) of the hydrated samples was minor. Statistical comparison using Student's *t* tests (unpaired, unequal variance) between the different hydration stoppage techniques indicate that carbonation was significantly higher for the oven dried Portland cement sample. Differences between the other techniques were not significant (at the $p = 0.05$ level). All *t* test matrices can be found in the Supplementary Material. Each set

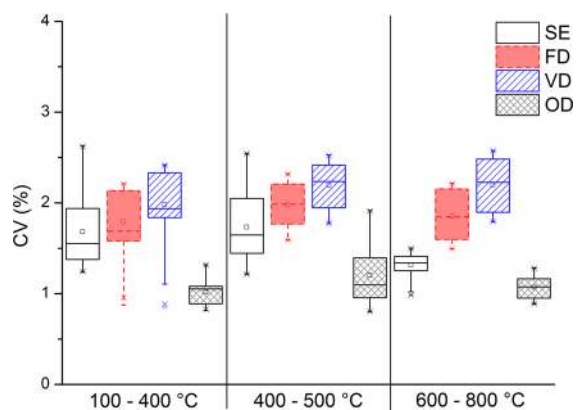


Fig. 3 Distributions of coefficients of variation of the TG raw data shown for each hydration stoppage technique across the main temperature intervals. *SE* solvent exchange, *FD* freeze drying, *VD* vacuum drying and *OD* oven drying. Values are shown for: the median (middle bar in box), mean (square), 25–75% quartile intervals (box), 1–99% intervals (whiskers) and minimum and maximum values (crosses)

of raw data contained one or more outlier curves that showed signs of sample carbonation. Some participants more frequently reported carbonation of samples, indicating that laboratory conditions (laboratory temperature and humidity) and technical proficiency, care (exposure during curing, sampling or storage), and the time between stoppage and analysis were additional causes of carbonation.

In a second step, the interlaboratory variation of the TG raw data for each hydration stoppage protocol is assessed. The distributions of the coefficients of variation per temperature interval in Fig. 3 show the highest reproducibility for oven drying, followed by solvent exchange. Freeze and vacuum drying showed the lowest reproducibility. The raw data for each of the hydration stoppage methods are given in Figs. 4, 5, 6 and 7. Averaged curves, when available, were given per participant. For analysis purposes all datasets were linearly interpolated on a 1 °C basis. Based on the interpolated curves an average was calculated and 95% (2σ) confidence intervals were constructed under the assumption of a normal distribution of error, the number of individual observations equals the number of participants reporting data for the concerned protocol (cf. Table S1).

The low reproducibility of the freeze and vacuum drying results is notable since the raw data for vacuum and freeze drying within each laboratory showed much less variation. Figure 8 illustrates this observation by plotting corresponding TG weight losses for vacuum and freeze drying for individual participants.

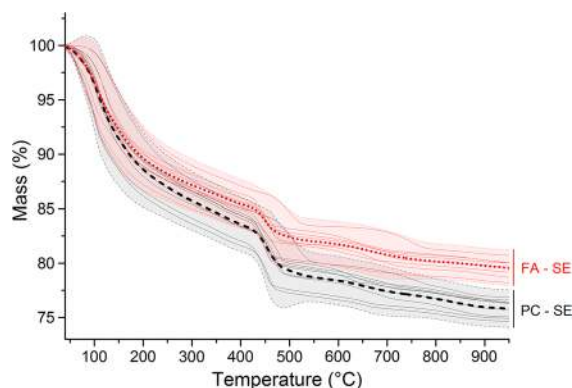


Fig. 4 Comparison of the TG curves from 10 laboratories of samples of which the hydration was stopped by solvent exchange (*SE*). The raw data are shown together with an average curve (bold lines) and 95% confidence intervals (shaded area)



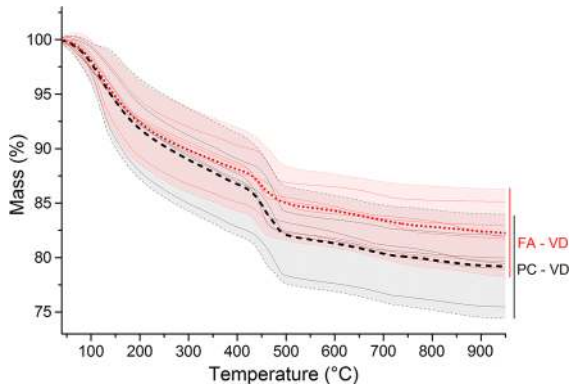


Fig. 5 Comparison of the TGA curves from 4 laboratories of samples of which the hydration was stopped by vacuum drying (VD). The raw data are shown together with an average curve (bold lines) and 95% confidence intervals (shaded area)

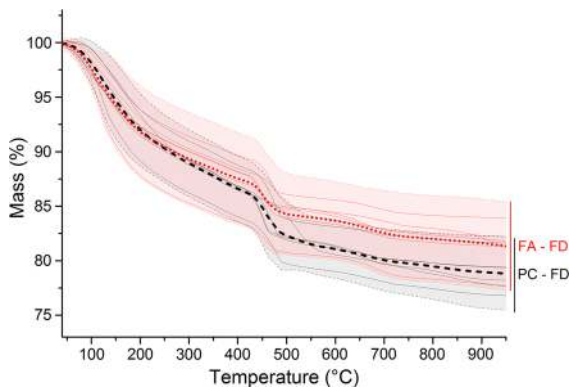


Fig. 6 Comparison of the TGA curves from 7 laboratories of samples of which the hydration was stopped by freeze drying (FD). The raw data are shown together with an average curve (bold lines) and 95% confidence intervals (shaded area)

The plot shows rather repeatable trends per participant (averaged curves where available), however interlaboratory reproducibility is poor. The measurements mainly diverge over the lower temperature range of 50–300 °C. This observation suggests that there is considerable variation in the efficacy of the used vacuum/freezing drying equipment in the removal of bound water. It is likely that different designs and/or operating conditions (vacuum level and/or temperature) result in significant variations in water vapor pressure.

In contrast to TG data a straightforward comparison of the raw XRD data of all was hindered by data quality. The differences in type and settings of the lab diffractometers resulted in large differences in

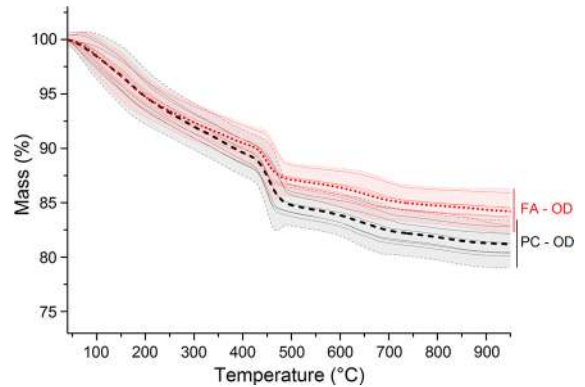


Fig. 7 Comparison of the TGA curves from 9 laboratories of samples of which the hydration was stopped by oven drying (OD) at 105 °C. The raw data are shown together with an average curve (bold lines) and 95% confidence intervals (shaded area)

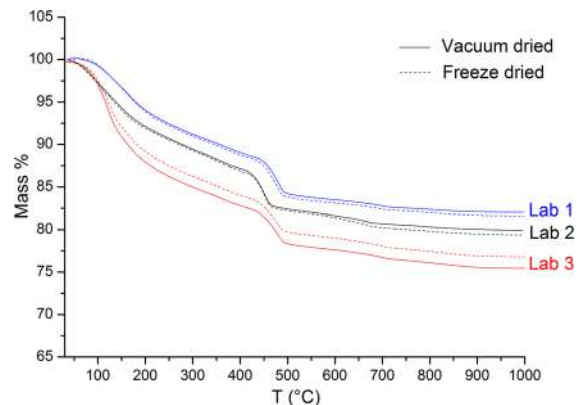


Fig. 8 Plot of weight loss measurements for vacuum dried and freeze dried samples for 3 participants

intensities and signal to noise ratios. Undoubtedly this reflects the important advances in XRD hardware, in particular detector technologies, that occurred over the last decades. Simple comparison by rescaling of the XRD data to similar peak heights could not be done because data of lower signal to noise ratio would obscure data with better resolution. Therefore the raw XRD data from all participants are not shown and instead, Fig. 9 plots XRD data from 1 participant over the 5°–30° 2θ (CuK α) range for the different treatments. The effects of the hydration stoppage methods on the XRD pattern were evaluated by comparison to a fresh, i.e. undried, sample that was cut as slice and immediately measured by XRD.

The most noticeable difference between the diffraction patterns shown is in the Bragg peaks of the

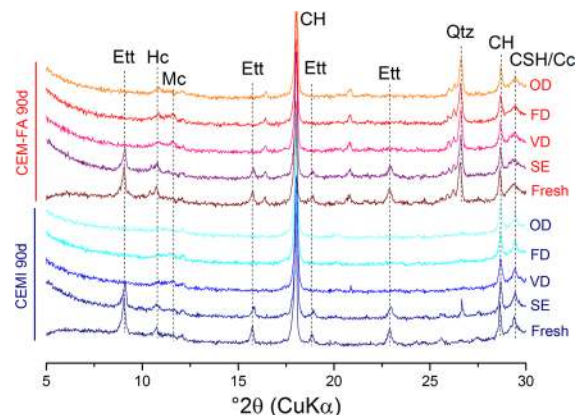


Fig. 9 Comparison of the XRD scans amongst the tested hydration stoppage methods for 1 participating laboratory (EPFL). Fresh: undried, *SE* solvent exchange, *VD* vacuum dried, *FD* freeze-dried, *OD* oven dried at 105 °C. The main peaks are assigned to *Ett* ettringite, *Hc* hemicarbonate, *Mc* monocarbonate, *CH* portlandite, *Qtz* quartz, *CSH* C–S–H and *Cc* calcite

ettringite and AFm phases. Clearly, crystalline ettringite is decomposed by oven drying, freeze drying and vacuum drying, confirming previous findings in the literature [10, 12]. Also after the solvent exchange treatment the main ettringite peak is clearly lowered. The AFm phases show a shift from hemicarbonate in the fresh sample towards monocarbonate for oven, freeze and vacuum dried samples. Least change from the fresh sample was again noted for the solvent exchange treated samples. Other Bragg peaks were much less affected by the method of hydration stoppage.

5.2 Results of the data analysis

All participants calculated bound water content and $\text{Ca}(\text{OH})_2$ content from the TG data according to the analysis guidelines in 4.5. The resulting values were assembled in Figs. 10 and 11, respectively. Box plots are used to show the spread on the reported results. Student *t* test calculations were made to support statements on statistical significance, the results are given in the Supplementary Material. The plots are organized to show for both hydrated samples the assembled results of each hydration stoppage method.

In case of the bound water content the results supported the observations made on the raw TG data. Bound water contents were significantly higher for solvent exchanged samples and the spread on the

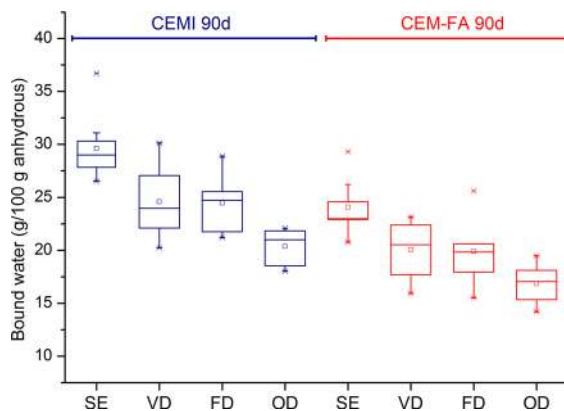


Fig. 10 Round robin test results of bound water content for both cement systems hydrated for 90 days. The results are represented by box plots grouped per hydration stoppage method (*SE* solvent exchange, *VD* vacuum drying, *FD* freeze drying, *OD* oven drying). Values are shown for: the median (middle bar in box), mean (square), 25–75% quartile intervals (box), 1–99% confidence intervals (whiskers) and minimum and maximum values (crosses)

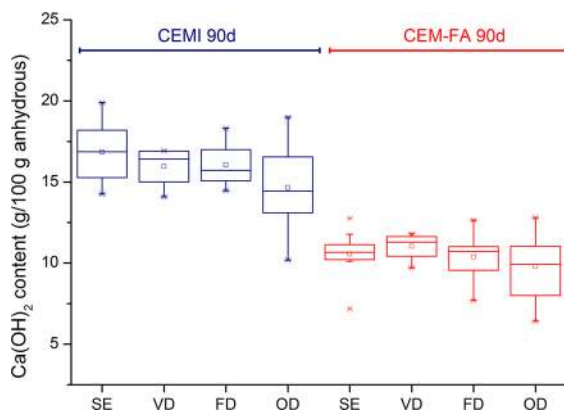


Fig. 11 Round robin test results of $\text{Ca}(\text{OH})_2$ content as measured by TGA for both cement systems hydrated for 90 days. The results are represented as box plots grouped per hydration stoppage method (*SE* solvent exchange, *VD* vacuum drying, *FD* freeze drying, *OD* oven drying). Values are shown for: the median (middle bar in box), mean (square), 25–75% quartile intervals (box), 1–99% confidence intervals (whiskers) and minimum and maximum values (crosses)

results was smallest for solvent exchange. The bound water contents of vacuum or freeze dried samples were not significantly different. A slightly larger spread on the data was found for the vacuum drying method. Oven drying invariably resulted in the lowest bound water contents (significantly lower than the others) while the spread on the reported results was moderate. In terms of total bound water content the hydration

stoppage methods are ordered as follows: solvent exchange > vacuum drying \approx freeze drying > oven drying. This is in line with previous findings [2, 11]. In terms of interlaboratory reproducibility of bound water content the hydration stoppage methods are ordered from most to least reproducible as follows: solvent exchange > oven drying > freeze drying > vacuum drying.

The tangential approach was used for $\text{Ca}(\text{OH})_2$ quantification. This approach is assumed to correct for the background loss of hydroxyls by other hydrates over the $\text{Ca}(\text{OH})_2$ dehydroxylation interval. Overall, reported $\text{Ca}(\text{OH})_2$ contents were similar for all hydration stoppage methods, differences were not statistically significant. Results for oven dried samples consistently showed the largest spread on $\text{Ca}(\text{OH})_2$ content, and median and mean values were slightly below that of other stoppage methods. Below average outliers invariably showed clear indications of carbonation. Oven dried samples were more prone to carbonate, likely because of prolonged exposure to air flow. Interlaboratory reproducibility was similar for the tested solvent exchange, vacuum drying and freeze drying methods in case of $\text{Ca}(\text{OH})_2$ content quantification by TG.

Rietveld analysis was carried out by all participants to calculate portlandite and ettringite contents from the raw XRD data. Compared to TG analysis, Rietveld analysis is a much more complex process that demands considerable experience by the operator [13, 14]. Operator choices were limited as much as possible by supplying clear instructions and starting values for the refinement. However, due to differences in data quality, software architecture and fitting routines, and sample manipulation the reproducibility of the quantification results was much poorer than for TG.

Reported portlandite contents were similar in terms of median and mean values for all hydration stoppage methods (Fig. 12). The interlaboratory reproducibility was found to be best for solvent exchange, all other methods performing similarly. Notably portlandite contents determined by XRD were consistently higher than $\text{Ca}(\text{OH})_2$ contents determined by TG. In case of the hydrated Portland cement XRD reported values were on average 4–5 wt% higher than $\text{Ca}(\text{OH})_2$ determined by TG. In the fly ash blended cement the difference was smaller, i.e. about 2 wt%, and within acceptable error. When the overall degree of hydration of the main clinker phases is taken into account the

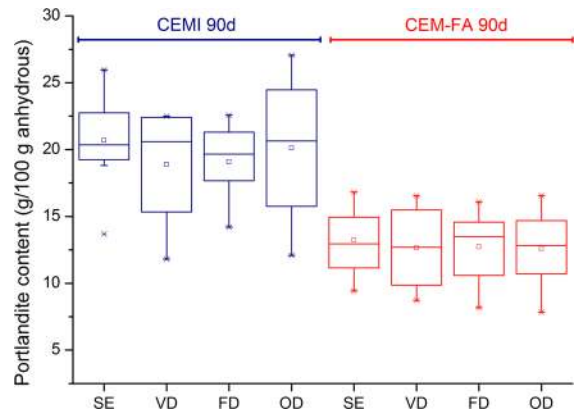


Fig. 12 Round robin test results of portlandite content as measured by XRD for both cement systems hydrated for 90 days. The results are represented as box plots grouped per hydration stoppage method (SE solvent exchange, VD vacuum drying, FD freeze drying, OD oven drying). Values are shown for: the median (middle bar in box), mean (square), 25–75% quartile intervals (box), 1–99% confidence intervals (whiskers) and minimum and maximum values (crosses)

portlandite levels calculated by mass balance are much more in line with the XRD results, not with the TG results. There thus appears to be a systematic error in the TG data analysis. Carbonation of portlandite during the measurement can only explain the difference to some extent (1–2 wt%). In addition, a hint to explaining the discrepancy found for Portland cement may reside in the observation that in mixes of pure C–S–H and portlandite, the dehydrated C–S–(H) appears to be able to resorb or react with part of the water vapour released during portlandite decomposition (A. Muller and P. Durdzinski, unpublished results). Part of this water (hydroxyls) is then only slowly released later, contributing to the slight slope of the TG curves above 500 °C. This process would also lead to an underestimation of the $\text{Ca}(\text{OH})_2$ level by TG.

The reported ettringite contents in Fig. 13 clearly show that ettringite persisted in solvent exchanged samples, while for all other hydration stoppage methods only traces of ettringite were found. This is in line with the reduced bound water contents for the direct drying methods and the well-known desintegration of ettringite at low relative humidity or temperatures above 50 °C [12, 15]. The large spread of reported ettringite contents in solvent exchanged samples reflects that also the tested solvent exchange procedure cannot entirely avoid ettringite decomposition. This is further supported by Fig. 14 in which the

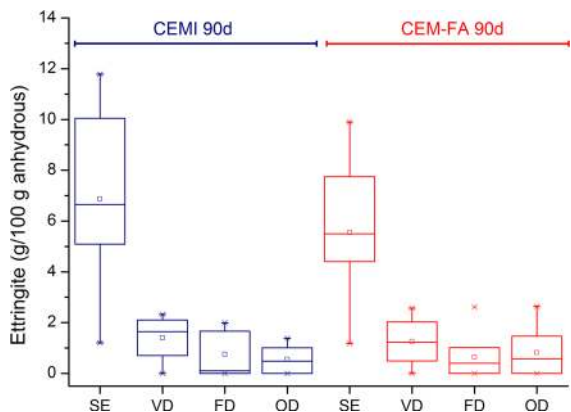


Fig. 13 Round robin test results of ettringite content as measured by XRD for both cement systems hydrated for 90 days. The results are represented as box plots grouped per hydration stoppage method (*SE* solvent exchange, *VD* vacuum drying, *FD* freeze drying, *OD* oven drying). Values are shown for: the median (middle bar in box), mean (square), 25–75% quartile intervals (box), 1–99% confidence intervals (whiskers) and minimum and maximum values (crosses)

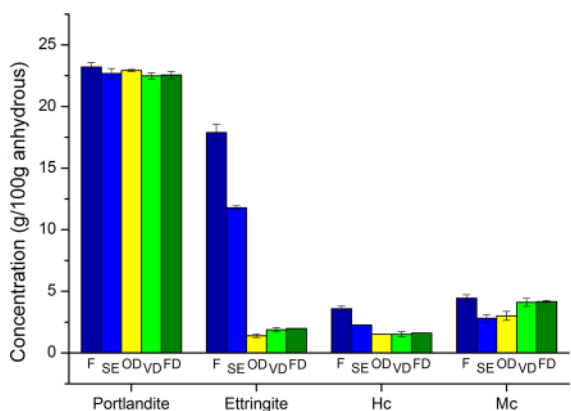


Fig. 14 XRD-Rietveld analysis results (EPFL) comparing the effect of hydration stoppage methods on the quantification of portlandite, ettringite, hemicarboaluminate (Hc) and monocarboaluminate (Mc). As a reference the analysis results for a fresh, non-dried, disc sample (F) is given as well. *SE* solvent exchange, *VD* vacuum dried, *FD* freeze-dried, *OD* oven dried at 105 °C. Errors shown are repeatability errors (one standard deviation, for two samples)

comparison is made with ettringite levels in a sample measured in the fresh, undried state. Recent work indicated that structural decomposition of ettringite by solvent exchange can be reduced using cold (− 18 to 5 °C) isopropanol as main solvent [16]. Figure 14 also reports errors by interlaboratory repeatability, which are clearly much smaller than interlaboratory reproducibility error estimates. Moreover, also at the

individual laboratory level portlandite levels were not significantly changed by hydration stoppage, nor dependent on the hydration stoppage method. Hemicarbonate levels were higher in the fresh samples compared to the hydration stopped samples, monocarbonate levels were found to be similar.

6 Conclusions and recommendations

This paper reports the results of a round robin test on the effect of different hydration stoppage methods on the composition of hydrated cements. Ten laboratories participated in the round robin test. Protocols were established and tested for four common hydration stoppage methods: i.e. solvent exchange by isopropanol, vacuum drying, freeze drying and oven drying. A Portland cement and a fly ash blended cement hydrated for 90 days were subjected to testing. The hydration stopped powders were measured by TG and XRD for compositional analysis. Analysis guidelines were established to determine bound water and $\text{Ca}(\text{OH})_2$ content based on the TG data, and to quantify portlandite and ettringite content by Rietveld analysis of the XRD data. The aim was (1) to test interlaboratory reproducibility and (2) to identify problems, including artefacts, regarding the use of the selected hydration stoppage methods for the study of hydrate assemblages.

The interlaboratory reproducibility of the hydration stoppage methods was assessed according to the assessed material property and ordered from most to least reproducible:

- Bound water content (TG): solvent exchange \approx oven drying > freeze drying > vacuum drying.
- $\text{Ca}(\text{OH})_2$ content (TG): solvent exchange \approx freeze drying \approx vacuum drying > oven drying.
- Portlandite content (XRD): solvent exchange > freeze drying \approx vacuum drying \approx oven drying.
- Ettringite content (XRD): best by solvent exchange, ettringite was decomposed by the other methods.

Overall, solvent exchange comes out best in terms of reproducibility of the analysis results. Interlaboratory reproducibility was best for TG analysis compared to XRD analysis, and better for $\text{Ca}(\text{OH})_2$ than bound water content measurements. The former is related to the larger variability in XRD raw data

quality and the more complex quantification procedure in case of Rietveld analysis. The latter is explained by the larger sensitivity of bound water content to changes in the hydration stoppage treatment.

In evaluating potential issues and artefacts of the tested methods, following conclusions are drawn.

- The solvent exchange method best preserved the hydration product assemblage. It removed less bound water than the direct drying methods and kept ettringite best preserved.
- Oven drying at 105 °C performed worst in terms of preserving the hydrate assemblage. Most bound water was removed and ettringite, monosulfate and hemicarbonate were decomposed. Moreover, oven dried samples showed significantly higher carbonation.
- Vacuum and freeze drying had similar and intermediate effect in terms of bound water removal. Ettringite was largely decomposed by both treatments. It should be noted that varying operational performance of the vacuum and freeze drying equipment used by the participants caused a relatively large spread on the reported results.

Following recommendations are made based on the results of the round robin test:

1. Oven drying at 105 °C is not recommended. This dehydrated, altered and decomposed calcium aluminate hydrates significantly more than other methods and was significantly more prone to carbonation.
2. Isopropanol exchange with an exchange period limited to 15 min for crushed powders was most appropriate for the study of the complete hydrate assemblage of cements, including calcium aluminate hydrates such as ettringite and AFm phases.
3. For quantification of portlandite ($\text{Ca}(\text{OH})_2$) all tested hydration stoppage protocols were satisfactory, except oven drying which may cause carbonation artefacts.

Acknowledgements This work was carried out as part of the activities of RILEM Technical Committee 238-SCM on Supplementary Cementitious Materials. Maria Juenger is gratefully acknowledged for the detailed review that considerably improved the paper. As Postdoctoral Research Assistant of the Research Foundation-Flanders (FWO-

Vlaanderen), Didier Snoeck wants to thank the foundation for its financial support.

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Winnefeld F, Schöler A, Lothenbach B (2016) Sample preparation. In: Scrivener KL, Snellings R, Lothenbach B (eds) A practical guide to microstructural analysis of cementitious materials. CRC Press, Boca Raton, pp 1–36
2. Zhang J, Scherer GW (2011) Comparison of methods for arresting hydration of cement. *Cem Concr Res* 41(10):1024–1036. <https://doi.org/10.1016/j.cemconres.2011.06.003>
3. Korpa A, Trettin R (2006) The influence of different drying methods on cement paste microstructures as reflected by gas adsorption: comparison between freeze-drying (F-drying), D-drying, P-drying and oven-drying methods. *Cem Concr Res* 36(4):634–649. <https://doi.org/10.1016/j.cemconres.2005.11.021>
4. Collier NC, Sharp JH, Milestone NB, Hill J, Godfrey IH (2008) The influence of water removal techniques on the composition and microstructure of hardened cement pastes. *Cem Concr Res* 38(6):737–744. <https://doi.org/10.1016/j.cemconres.2008.02.012>
5. Snoeck D, Velasco LF, Mignon A, Van Vlierberghe S, Dubruel P, Lodewyckx P, De Belie N (2014) The influence of different drying techniques on the water sorption properties of cement-based materials. *Cem Concr Res* 64:54–62. <https://doi.org/10.1016/j.cemconres.2014.06.009>
6. Knapen E, Cizer O, Van Balen K, Van Gemert D (2009) Effect of free water removal from early-age hydrated cement pastes on thermal analysis. *Constr Build Mater* 23(11):3431–3438
7. Gallé C (2001) Effect of drying on cement-based materials pore structure as identified by mercury intrusion porosimetry. A comparative study between oven-, vacuum-, and freeze-drying. *Cem Concr Res* 31:1467–1477
8. Schöler A, Lothenbach B, Winnefeld F, Zajac M (2015) Hydration of quaternary Portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder. *Cement Concr Compos* 55:374–382. <https://doi.org/10.1016/j.cemconcomp.2014.10.001>
9. Snellings R (2016) X-ray powder diffraction applied to cement. In: Scrivener KL, Snellings R, Lothenbach B (eds) A practical guide to microstructural analysis of cementitious materials. CRC Press, Boca Raton, pp 107–176
10. Zhang L, Glasser F (2000) Critical examination of drying damage to cement pastes. *Adv Cem Res* 12(2):79–88
11. Lothenbach B, Durdzinski P, De Weerd K (2016) Thermogravimetric analysis. In: Scrivener KL, Snellings R, Lothenbach B (eds) A practical guide to microstructural

- analysis of cementitious materials. CRC Press, Boca Raton, pp 179–213
12. Baquerizo LG, Matschei T, Scrivener KL (2016) Impact of water activity on the stability of ettringite. *Cem Concr Res* 79:31–44
 13. León-Reina L, De la Torre A, Porras-Vázquez J, Cruz M, Ordonez L, Alcobé X, Gispert-Guirado F, Larrañaga-Varga A, Paul M, Fuellmann T (2009) Round robin on Rietveld quantitative phase analysis of Portland cements. *J Appl Crystallogr* 42(5):906–916
 14. Madsen IC, Scarlett NV, Cranswick LM, Lwin T (2001) Outcomes of the International Union of Crystallography Commission on powder diffraction round robin on quantitative phase analysis: samples 1a to 1h. *J Appl Crystallogr* 34(4):409–426
 15. Lothenbach B, Matschei T, Möschner G, Glasser FP (2008) Thermodynamic modelling of the effect of temperature on the hydration and porosity of Portland cement. *Cem Concr Res* 38(1):1–18. <https://doi.org/10.1016/j.cemconres.2007.08.017>
 16. Mantellato S, Palacios M, Flatt RJ (2016) Impact of sample preparation on the specific surface area of synthetic ettringite. *Cem Concr Res* 86:20–28