

Outcomes of the RILEM round robin on degree of reaction of slag and fly ash in blended cements

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Abstract Working group 2 of the RILEM TC 238-SCM undertook a comparison of laboratories and techniques for the quantification of the degree of reaction of supplementary cementitious materials in blended cements. A common set of binary pastes of Portland cement with two slags, a calcareous and a siliceous fly ash was tested in seven laboratories. The results obtained by selective dissolution produced were quite scattered and seemed to underestimated the degree of reaction. The analysis of portlandite consumption was found to significantly underestimate the reaction unless additional data from XRD and electron microscopy was gathered to complete the corrections. Despite limited access to electron microscope among

the participants and thus only a small data set being collected, this technique appeared as one of the most consistent. XRD-PONKCS gave considerable scatter, due mainly to a lack of a strict protocol and excessive overlap of slag and C–S–H signals. Overall, the study indicated that the precision of determination of the degree of reaction of SCMs in cement pastes is rather low and at best $\pm 5\%$.

Keywords Supplementary cementitious materials · Degree of reaction · Selective dissolution · Thermogravimetry · X-ray powder diffraction with Rietveld refinement · Electron microscopy image analysis

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1 Introduction

Working group 2 of the RILEM TC 238-SCM: Hydration and microstructure of concrete with supplementary cementitious materials (SCMs) undertook a comparison of several methods in several laboratories, to determine the degree of reaction of slag and fly ash in composite cements. The quantification of the degree of reaction of SCMs in hydrating cement is challenging and each of the available methods has strengths and weaknesses. The currently available methodologies were recently summarized and reviewed by the committee in [1], but their actual inter-laboratory variation has never been tested. For this study four techniques were chosen: (1) selective dissolution using EDTA for slag cements and salicylic acid + HCl for fly ash cements, (2) analysis of the consumption of portlandite content measured by thermogravimetry (TG), (3) X-ray powder diffraction (XRD) with PONKCS refinement (partial or no known crystal structure) and (4) scanning electron microscopy with image analysis (SEM-IA).

Selective dissolution of composite cement pastes aims to dissolve all paste components except the unreacted SCM, which can then be quantified. In practice, a part of the slag or fly ash is dissolved while some hydrates and unreacted clinker remain. In [1] it was concluded that significant, non-quantifiable, systematic errors generally lead to a spread in results.

The analysis of the consumption of portlandite attempts to calculate the degree of reaction of the SCM from the amount of portlandite consumed in its reaction in portland cement. The portlandite consumed is measured by thermogravimetry. The degree of reaction of the SCM is then calculated based on the stoichiometric amount of silica required from the SCM to react with the portlandite. The errors are mainly related to the fact that (1) the Ca/Si ratio of the C–S–H decreases in the presence of reacting SCMs from around 1.8 in PC to 1.6 for slag cements [2] and 1.3 for fly ash cements [3], and (2) that the calculation of the degree of reaction is sensitive to variation of the measured portlandite content and Ca/Si ratio of the C–S–H.

SEM-IA of epoxy impregnated polished sections uses backscatter electron images (BSE) and EDS maps of the content of elements to extract areas in the images that correspond to anhydrous SCMs. The area fraction of anhydrous SCMs in images is equal to their

volume fraction in the paste and is thus used to calculate the degree of reaction. The critical issue lies in an accurate segmentation of the images. The grey level of the SCMs in BSE images is often similar to that of the hydrates and supplementary information may be required from EDS maps of selected elements. Slags are rich in Mg, which facilitates their separation in the images, but more sophisticated selection thresholds are needed to segment fly ash, with calcareous fly ash being the most difficult [4]. Overestimation of the degree of reaction may occur, due to the presence of fine SCM particles, below or around the resolution of the microscope and because in images, the captured sections of 3D features appear mostly smaller than the equatorial sections [5].

By coupling PONKCS [6] to XRD-Rietveld analysis, different amorphous materials can be quantified from their diffuse scattering ‘hump’. A separate scan of the amorphous component is used to calibrate a model, which relates the diffraction signal of this component to its content. An assessment of this relatively new technique to quantify SCMs in model mixes of slag, metakaolin, quartz and hydrated white cement showed good accuracy (2–3 wt%) and precision (around 1 wt%) [7]. In real blended systems, however, partial or entire overlap of the SCM ‘hump’ with that of the main amorphous hydrate C–S–H may lead to important errors [1].

Binary pastes of Portland cement with two slags, a calcareous and a siliceous fly ash, were prepared by one laboratory and sent out to other participants for analysis. As each participant followed their own protocols, the analysis of the collective data gave an idea of the maximum inter-laboratory variability in the results, which should be universally applicable. This study assesses the accuracy, precision and feasibility of application of the four selected techniques to determine degree of reaction of slag or fly ash in composite cements.

2 Participants

Seven laboratories participated in this round robin test:

- Laboratory of Construction Materials, EPFL, Switzerland
- HeidelbergCement Technology Center GmbH, Germany



- Department of Materials Science and Engineering, The University of Sheffield, UK
- Magnel Laboratory for Concrete Research, Ghent University, Belgium
- Laboratory for Concrete and Construction Chemistry, Empa, Switzerland
- Institute of Building Materials Research, RWTH Aachen University, Germany
- Eduardo Torroja Institute of Construction Science (IETcc-CSIC), Spain

The participants were given the freedom to choose the techniques to apply and to follow their own protocols. The laboratories were assigned random letters A–G.

3 Materials

The materials used for the study were Portland cement (PC), two slags (S1 and S2), siliceous fly ash (SFA), calcareous fly ash (CFA) and quartz (*Q*). The chemical composition and the phase composition of the anhydrous materials are given in Table 1. The XRD-Rietveld refinement of clinker phases in anhydrous PC was aided by analysis of samples treated with salicylic acid/methanol (SAM) and with KOH/sucrose. The two slags investigated were >99% amorphous and of very similar chemical composition. The particle size distributions of the anhydrous materials were measured by laser diffraction in isopropanol suspensions using a Malvern MasterSizer S. Refractive indices were calculated based on the chemical composition of the raw materials as $n_{PC} = 1.73$, $n_{S1} = n_{S2} = 1.70$, $n_{CFA} = 1.77$, $n_{SFA} = 1.60$, $n_{Quartz} = 1.54$ and the refractive index of isopropanol was $n_{solvent} = 1.39$. Absorption index was $k = 0.1$. The results are presented in Fig. 1.

The study was carried out using paste samples, all of which were prepared by one laboratory. Binary composite cements were prepared with PC and 40 wt% slag (PC-S1 and PC-S2) or 30 wt% fly ash (PC-SFA and PC-CFA). Reference samples included neat PC and mixes of PC with 40 and 30 wt% quartz inert filler (PC-Q40 and PC-Q30 respectively). The powders in portions of 80 g were mixed with water at water/binder ratio 0.4 in 150 mL plastic containers using a laboratory mixer at 1600 rpm for 2 min. The pastes were cast in cylindrical polypropylene containers of 33 mm internal diameter and sealed-cured for 1,

7, 28 and 90 days. Additional samples were demoulded after 1 day and water-cured until 28 and 90 days in slightly larger containers topped up with a minimal amount of water. After curing, discs of around 2–3 mm thickness and 33 mm diameter were cut from the paste cylinders. These discs were stored in lots of six per 200 mL of isopropanol for 7 days to stop hydration by solvent exchange. The isopropanol was replaced after 1 and 3 days of storage. The discs were then kept in vacuum desiccators (approx. 7 mbar) for 7 days to remove the isopropanol. After that, the samples were sealed in vacuum bags and sent out to the participants. The participants removed an outer layer of material from the samples by gentle grinding prior to testing, as it may have carbonated during the transport and storage.

4 Methods

- 4.1 Selective dissolution of slag cement pastes with EDTA + TEA + DEA (D, E, F, G) and of fly ash cement pastes with salicylic acid + HCl (D, E)

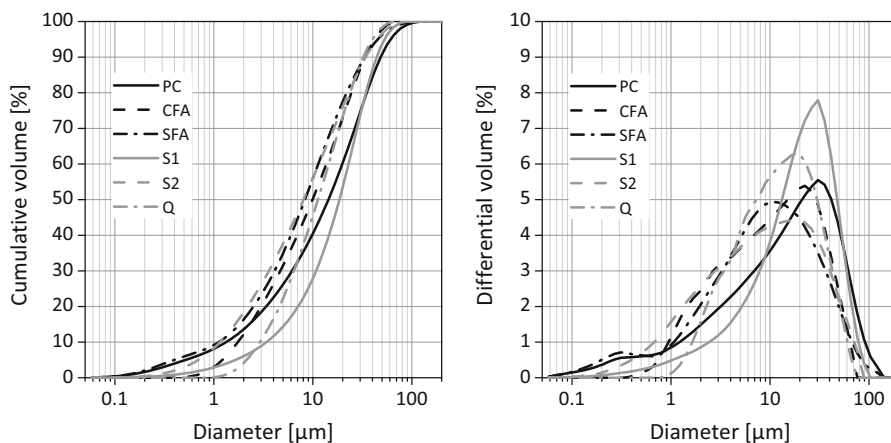
Selective dissolution was carried out in triplicate on anhydrous slags and fly ashes and on all their pastes. Prior to dissolution the samples were ground to <125 μm in lab D, <63 μm in lab E, and <90 μm in lab F.

The dissolution of anhydrous cement, slags, fly ashes and the neat PC paste was carried out to determine the undissolved residue of these materials, which, in the perfect case, should be zero for the Portland cement and its paste and 100 wt% for the SCMs. Details of the dissolution procedures are provided in further parts of this section. The results given in Table 2 show that 90–95 wt% of slags S1 and S2 remained undissolved, which value is rather low, but still acceptable. The residue of siliceous ash SFA was close to 100 wt%. From CFA, however, only 70–80 wt% remained undissolved, which makes it unacceptable for the determination of the degree of reaction by this method.

Unreacted slag and PC-S paste triplicate samples were subjected to EDTA-TEA-DEA attack. Based on the procedure described by Lumley et al. [8], 93.0 g of disodium EDTA + 250 mL of TEA + 500 mL of water + 173 mL of DEA were mixed and made up to

Table 1 Bulk chemical composition by X-ray fluorescence and phase composition by XRD-Rietveld refinement (wt%)

	S1	S2	CFA	SFA	PC	Q		CFA	SFA	PC
Al ₂ O ₃	11.6	11.6	19.8	24.4	5.7	1.0	C ₃ S	–	–	66.2
SiO ₂	36.5	36.7	42.3	70.8	19.3	97.9	C ₂ S	2.5	–	7.0
CaO	40.8	38.9	20.7	0.1	63.7	0.0	C ₃ A	1.0	–	6.5
Na ₂ O	0.5	0.2	0.3	0.1	0.2	–	C ₄ AF	1.6	–	11.9
K ₂ O		0.7	1.5	0.6	1.2	0.8	Quartz	1.3	14.9	0.2
MgO	7.5	7.8	2.2	0.2	1.6	–	Calcite	–	–	0.7
Fe ₂ O ₃	1.4	0.5	8.2	2.2	3.6	0.0	Dolomite	–	–	0.4
SO ₃	2.1	2.8	1.4	–	3.2	–	Mullite	–	19.3	–
TiO ₂	–	0.9	0.7	1.5	0.3	0.0	CaO	1.7	–	–
P ₂ O ₅	–	–	0.3	0.1	0.2	0.0	Ca(OH) ₂	1.6	–	0.2
Mn ₂ O ₃	–	–	–	0.1	0.1	–	Anhydrite	1.8	–	4.6
LOI 1050 °C	–	–	1.1	–	0.8	0.2	Arcanite	–	–	2.1
							Periclase	–	–	0.2
							Magnetite	1.3	–	–
Sum	100.4	100.1	98.5	100.1	99.9	99.9	Amorphous	87.2	65.8	–

Fig. 1 Particle size distributions determined by laser diffraction**Table 2** Residues after selective dissolution of the anhydrous materials and the Portland cement paste (wt%)

Laboratory	D	E	F
<i>EDTA + TEA + DEA</i>			
Anhydrous cement	0.4 ± 0.1	0.4 ± 0.1	0.1 ± 0.1
PC paste	1.3 ± 0.4	–	–
S1	89.9 ± 1.1	95.0 ± 0.1	92.2 ± 0.5
S2	90.1 ± 0.5	95.2 ± 0.7	92.2 ± 0.5
<i>Salicylic acid + HCl</i>			
Anhydrous cement	1.2 ± 0.1	0.9 ± 0.1	–
PC paste	0.9 ± 0.2	0.8 ± 0.1	–
CFA	71.7 ± 0.4	79.48 ± 0.5	–
SFA	97.9 ± 0.3	99.7 ± 0.3	–

1000 mL with water. For each extraction test, 50 mL of the above solution was diluted to approximately 800 mL with water and brought to a temperature of 20.0 ± 2 °C. Then 0.50 ± 0.02 g of dried and ground sample paste was weighed to the nearest 0.0001 g and sprinkled over the surface of the solution. The mixture of the solution and the ground sample was stirred for 120 ± 5 min at the stated temperature. In laboratories D and E the dissolution residues were vacuum filtrated on pre-dried glass fibre filters, washed, dried at 105 °C and weighed. In laboratory F the residues were filtered under vacuum through a 90 mm diameter Whatman GF/C filter. This filter had been previously washed with 100 mL of distilled water, dried at 105 °C and weighed. The residue was washed 5 times with 10 mL lots of distilled water, dried at 105 °C for 1 h and weighed to the nearest 0.0001 g. The residues contained unreacted slag and undissolved hydrates, in particular hydrotalcite-like phases, which were accounted for as in [8] and the degree of reaction of slag α was computed as:

$$\alpha_{\text{slag}} = \frac{100fp - R_b + R_{\text{PC}}(1-f)}{f(100p - hM_s)} \times 100\% \quad (1)$$

f = Mass fraction of slag in initial dry blend = 0.4.
 p = Mass fraction of slag undissolved by EDTA.
 R_b = Mass of residue from the PC-S paste in g/100 g of anhydrous binder. R_{PC} = Mass of residue from the PC paste in g/100 g of anhydrous binder. h = Mass of dried hydrotalcite formed from 1 g of MgO in the slag glass = 2.35 g. M_s = Mass of MgO in the slag glass in g/100 g slag.

Unreacted fly ashes and PC-fly ash pastes in 2 ± 0.02 g samples were mixed for 30 min with 200 mL of HCl + salicylic acid + methanol, a method based on the European standard CEN/TR 196-4:2007 for the determination of the composition of anhydrous blended cements. The acid solution was prepared from 41 mL HCl and 50 mg salicylic acid, made up to 1000 mL with methanol. The dissolution residues were vacuum filtrated on pre-dried glass fibre filters, washed, dried at 105 °C and weighed. This treatment dissolves sulfate-bearing phases such as ettringite or monosulfate, which precipitate as gypsum and dehydrate to bassanite during the drying of the residue [9]. The SO_3 content in the residue needed for the sulfate correction was determined by the combustion infrared detection technique. Values expressed per 100 g of isopropanol-vacuum dried paste were

converted to per 100 g of anhydrous binder basis using bound water content measured by thermogravimetry (ignition loss at 600 °C):

$$m_{\text{per 100 g anhydrous binder}} = \frac{m_{\text{per 100 g paste}}}{(1 - m_{\text{H}_2\text{O bound}})} \quad (2)$$

$$= \frac{m_{\text{per 100 g paste}}}{m_{\text{TG residue at 600 °C}}}$$

The degree of reaction of fly ash α was calculated as:

$$\alpha_{\text{fly ash}} = \frac{100fp - R_b(1 - bS_b) + R_{\text{PC}}(1-f)(1 - bS_{\text{PC}})}{100fp} \times 100\% \quad (3)$$

f = Mass fraction of fly ash in initial dry binder = 0.3.

p = Mass fraction of fly ash undissolved by salicylic acid + HCl. R_b = Mass of residue from the PC-FA paste in g/100 g anhydrous binder. R_{PC} = Mass of residue from the PC paste in g/100 g anhydrous binder. b = Mass of bassanite formed from 1 g of $\text{SO}_3 = 1.813$ g. S_b = Mass of SO_3 in PC-FA paste residue in g/g of residue. S_{PC} = Mass of SO_3 in PC paste residue in g/g of residue.

4.2 Consumption of portlandite measured by thermogravimetry and analysed by mass-balance (A, B, C, D, E, F)

A summary of the setups used by the participants for thermogravimetric experiments is given in Table 6 (Appendix). In TG curves the mass loss around 450 °C was assigned to water from the dehydroxylation of portlandite. Because of the non-zero background in this temperature range, mainly due to water lost from C-S-H the mass loss from portlandite could not be quantified by a simple horizontal step. A tangential technique was used in two variants: (1) a tangential step, in which the mass difference is calculated at the inflection point of the DTG peak (A, D, F), and (2) a tangential step between the onset and the end of the DTG peak (B, C, E). The amount of portlandite was computed by multiplying the obtained mass loss by the ratio of molar mass of portlandite and of water (74.09/18.02) and was expressed per 100 g of anhydrous binder using Eq. (2).

Part of the CO_2 emitted during heating may come from carbonated portlandite, the amount of which can



be calculated and added to the amount of portlandite quantified from the water loss. In this study, laboratory D applied this correction, while others did not arguing that the samples had been treated with isopropanol, which may also contribute to the CO₂ emitted and thus result in errors.

The degree of reaction of the SCMs was calculated based on the difference in the amount of portlandite between PC-SCM and PC-Q30/Q40 pastes. The use of quartz filler as the reference aimed to correct for the physical effect of SCMs on the hydration of cement (filler effect), so the differences in portlandite should be related to the consumption of this phase by the reaction of the SCMs.

The mass-balance method assumes that all Si dissolved from the SCM precipitates as C–S–H and that Ca for this reaction is taken from portlandite and from the SCM itself. Thus, for 1 mol of Si reacted the number of moles of Ca needed from portlandite are equal to:

$$\frac{n_{\text{CH consumed}}}{n_{\text{Si, SCM reacted}}} = \left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{C-S-H}} - \left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{SCM}} \quad (4)$$

and the absolute number of moles of Si reacted is equal to:

$$n_{\text{Si, SCM reacted}} = \frac{\alpha}{100\%} f \frac{w_{\text{SiO}_2, \text{SCM}}}{M_{\text{SiO}_2}} \quad (5)$$

α = Degree of reaction of SCM in %. f = Mass fraction of SCM in initial dry blend, 0.3 for fly ash and 0.4 for slag. $w_{\text{SiO}_2, \text{SCM}}$ = Mass of silica in the reactive amorphous part of the SCM, in g/100 g of the SCM. M_{SiO_2} = Molar mass of silica = 60.08 g/mol.

The absolute number of moles of portlandite consumed by the SCM reaction is calculated from the thermogravimetric measurement, and taking into account for CFA also the portlandite present in this ash, and the portlandite that forms from the C₂S and free lime in it:

$$n_{\text{CH consumed}} = \frac{\Delta m_{\text{CH}}}{M_{\text{CH}}} + f \left(\frac{m_{\text{CH, SCM}}}{M_{\text{CH}}} + \frac{m_{\text{Lime, SCM}}}{M_{\text{CaO}}} + \frac{m_{\text{C}_2\text{S, SCM}}}{M_{\text{C}_2\text{S}}} \left(2 - \left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{C-S-H}} \right) \right) \quad (6)$$

Δm_{CH} = Difference in the mass of portlandite between PC-SCM and PC-Q30/Q40, expressed in g/100 g anhydrous binder. $m_{\text{CH, SCM}}$ = Mass of portlandite in 100 g unreacted SCM. $m_{\text{Lime, SCM}}$ = Mass of

free lime in 100 g unreacted SCM. $m_{\text{C}_2\text{S, SCM}}$ = Mass of C₂S in 100 g unreacted SCM. M_{CH} = Molar mass of portlandite = 74.09 g/mol. M_{CaO} = Molar mass of CaO = 56.08 g/mol. $M_{\text{C}_2\text{S}}$ = Molar mass of C₂S = 172.24 g/mol.

The value of 2 in the above equation corresponds to the Ca/Si ratio of C₂S. By combining Eqs. (4), (5) and (6), the degree of reaction can be expressed as:

$$\alpha = \frac{\frac{\Delta m_{\text{CH}}}{M_{\text{CH}}} + f \left(\frac{m_{\text{CH, SCM}}}{M_{\text{CH}}} + \frac{m_{\text{Lime, SCM}}}{M_{\text{CaO}}} + \frac{m_{\text{C}_2\text{S, SCM}}}{M_{\text{C}_2\text{S}}} \left(2 - \left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{C-S-H}} \right) \right)}{f \frac{w_{\text{SiO}_2, \text{SCM}}}{M_{\text{SiO}_2}} \left(\left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{C-S-H}} - \left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{SCM}} \right)} \times 100\% \quad (7)$$

The $\left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{SCM}}$ and $w_{\text{SiO}_2, \text{SCM}}$ were derived from the XRF bulk chemical composition data. For fly ashes, the theoretical composition of the reactive amorphous part was computed by subtracting from the bulk chemical composition the amounts of oxides corresponding to crystalline phases (Table 1). The reactive amorphous fraction was 0.872 for CFA and 0.658 for SFA. The $\left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{SCM}}$ and the $w_{\text{SiO}_2, \text{SCM}}$ were calculated from the theoretical composition of this fraction and are shown in Table 3.

For the calculation of the degree of reaction of SCMs from the portlandite consumption, it is necessary to know the Ca/Si ratio of the C–S–H. Published results [2, 3, 10, 11] show that the Ca/Si ratio of the C–S–H in blended cements decreases with the increase in the degree of reaction of the SCM. As shown in [11], there does exist a correlation between the amount of portlandite and the Ca/Si ratio of the C–S–H, from which the Ca/Si ratio could be estimated. However, the precision of such estimation is limited, as Ca/Si ratios of mixes containing similar amounts of portlandite shown in [11] tend to vary in the range of ± 0.1 . The scatter in the degree of reaction of SCM due to this uncertainty, depending

Table 3 Molar ratio of Ca/Si and mass of silica in the reactive amorphous part of the SCMs studied

Unit	S1	S2	CFA	SFA	
$\left(\frac{\text{Ca}}{\text{Si}}\right)_{\text{SCM}}$	–	1.199	1.136	0.375	0.001
$w_{\text{SiO}_2, \text{SCM}}$	g/100 g SCM	36.45	36.70	40.13	50.49



on hydration time and SCM, could reach 60% absolute (Sect. 5.3).

Thus, in this study the chemical composition of the C–S–H was measured by one of the laboratories following the SEM–EDS point analysis procedure of Famy et al. [12] recently improved by Rossen and Scrivener [13]. The results are shown in Table 4. It was difficult to obtain reliable data at 1 day of hydration, hence the Ca/Si ratios at 7-day hydration were also used for the analysis of the 1-day samples. The uncertainty of determination of Ca/Si ratio of the C–S–H using this technique was estimated to be around ± 0.05 .

The decreasing Ca/Si ratios in Table 4 indicate that besides the Ca from portlandite, a considerable amount of Ca incorporated into the C–S–H formed from the SCM hydration must be provided by the C–S–H formed at earlier stages of reaction. To correct for this effects, it is necessary to make an additional measurement of the degree of reaction of C_3S and C_2S from the clinker and this is discussed in Sect. 5.3. The potential consumption of Ca to form AFt/AFm phases was not taken into account.

4.3 SEM-image analysis (B, E)

Polished sections of epoxy-impregnated paste discs were coated with ~ 15 nm of conductive carbon and analysed using SEM-image analysis. Details of the setups are given in the appendix Table 7. Unreacted slag was quantified using BSE images and EDS maps of Mg (lab B) or Mg, Ca, Si (lab E) similarly to [14]. Unreacted fly ash was segmented using high quality EDS maps of all main elements present, as in [4]. The degree of reaction of the SCMs was computed as:

$$\alpha = \frac{S_0 - S_t}{S_0} \times 100\% \quad (8)$$

Table 4 Molar Ca/Si ratios of the C–S–H used for the calculation of the degree of reaction of SCMs from portlandite consumption

	1 day	7 days	28 days	90 days
PC-S1	1.82	1.82	1.77	1.72
PC-S2	1.82	1.82	1.75	1.72
PC-CFA	1.85	1.85	1.80	1.64
PC-SFA	1.85	1.85	1.76	1.64

Uncertainty of determination was estimated at ± 0.05

where S_0 is the initial fraction of the SCM and S_t is the fraction of unreacted SCM at time t .

4.4 XRD-PONKCS (A, B, C, E)

X-ray powder diffraction measurements were carried out on anhydrous SCMs and on ground pastes using the experimental setups summarized in Table 8 in appendix. Rietveld refinement with PONKCS analysis was carried out under conditions specified in Table 9 in appendix. The results of the refinements were recalculated to g/100 g anhydrous binder using Eq. (2).

5 Results and discussion

The degrees of reaction of the four SCMs studied are given in Table 5 and Fig. 2. In Fig. 2, the points correspond to the mean degree of reaction and the whiskers show min–max values. A global mean was calculated as an average of means.

5.1 Precision and accuracy of the techniques studied

Precision of a technique comprises the uncertainty of measurement due to the technique itself and due to the inter-laboratory scatter. Accuracy, on the other hand, demonstrates how far the results are shifted from the actual degree of reaction. Because the actual degree of hydration of the SCMs remains unknown, the accuracy can only be assessed by a comparison to the global mean and by analysing potential causes of under-/over-estimated results. This will be discussed for each technique separately in further sections.

In this section the precision is assessed using standard deviation, which was calculated for each technique independently of time and is presented in Fig. 3. The whiskers represent the 90% confidence interval of the standard deviation.

Figure 3 shows that, according to the data available in this study, if any other laboratory carries out e.g. an analysis of slag reaction using EDTA + TEA + DEA 90% of their results will fall within ± 8 absolute % of the result obtained in this study. Because of the scatter of the results and the limited amount of data in this study the confidence limits given in Fig. 3 are different



Table 5 Degrees of reaction of SCMs [%] measured by the techniques investigated

Lab.	S1						S2						CFA						SFA					
	1	7	28	90	28	90	1	7	28	90	28	90	1	7	28	90	28	90	1	7	28	90	28	90
Selective dissolution																								
<i>D</i>	16	33	44				25	37	41															
<i>E</i>	1	15	24	34	29	40	10	18	24	41	26	38	Not reliable, CFA too soluble in the acid mixture						6	4	19			
<i>F</i>	7	17	39	61	47	85													6	12	12	23		
<i>G</i>	9	16	32	31	37	38	18	25	38	34	41	34												
Portlandite consumption – mass balance																								
<i>A</i>	8	20	33	24	27	21	2	11	24	28	22	21	-2	2	15	18	9	23	0	0	5	8	4	8
<i>B</i>	7	23	19	33	29	20	4	18	27	31	26	23	3	8	10	27	14	18	2	3	3	12	5	11
<i>C</i>	9	20	21	30			5	15	26	21			3	8	14	15			2	4	8			8
<i>D</i>	11	26	45				16	26	35										1	6	12			
<i>E</i>	2	23	37	37	49	32	4	25	39	37	32	36	7	14	22	23	19	33	1	4	6	12	10	13
<i>F</i>	15	22	29	33	21	33	7	17	29	31	24	30	10	13	18	27	17	25	2	3	4	12	6	13
SEM-IA																								
<i>B</i>	15	36	48	50	51		16	32	45	54	52		1	11	23	43	38		3	10	20	25	28	
<i>E</i>	12	33	38	55	51	64	22	45	49	64	52	57												
XRD-PONKCS																								
<i>A</i>	-10	23	55	50	37	34																		
<i>B</i>	4	25	38	37	40	30	11	36	48	48	47	53	9	12	24	25	25	32	0	16	19	24	21	30
<i>C</i>	11	32	44	45			3	13	22	33	33		19	24	48	46			5	17	22	25		
<i>E</i>	2	34	91	82	64	96	-12	44	56	99	86	89	-3	11	23	16	34	58	14	15	23	30	18	36

Italicised columns correspond to water-cured samples. Selective dissolution of slags was based on EDTA + TEA + DEA and that of fly ashes on salicylic acid + HCl



Fig. 2 Comparison of mean and min–max (whiskers) degrees of SCM reaction measured. Selective dissolution did not work for the calcareous fly ash (PC-CFA) and for this material only one series of SEM-IA results was reported. The results for water-cured samples are not shown

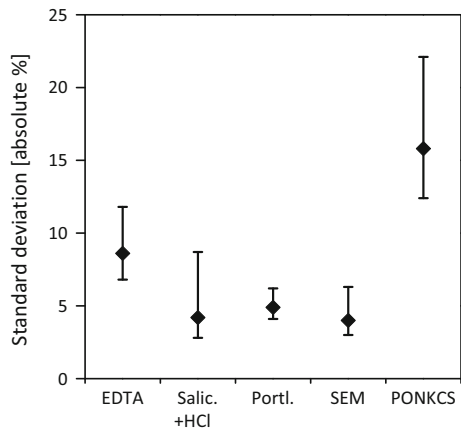
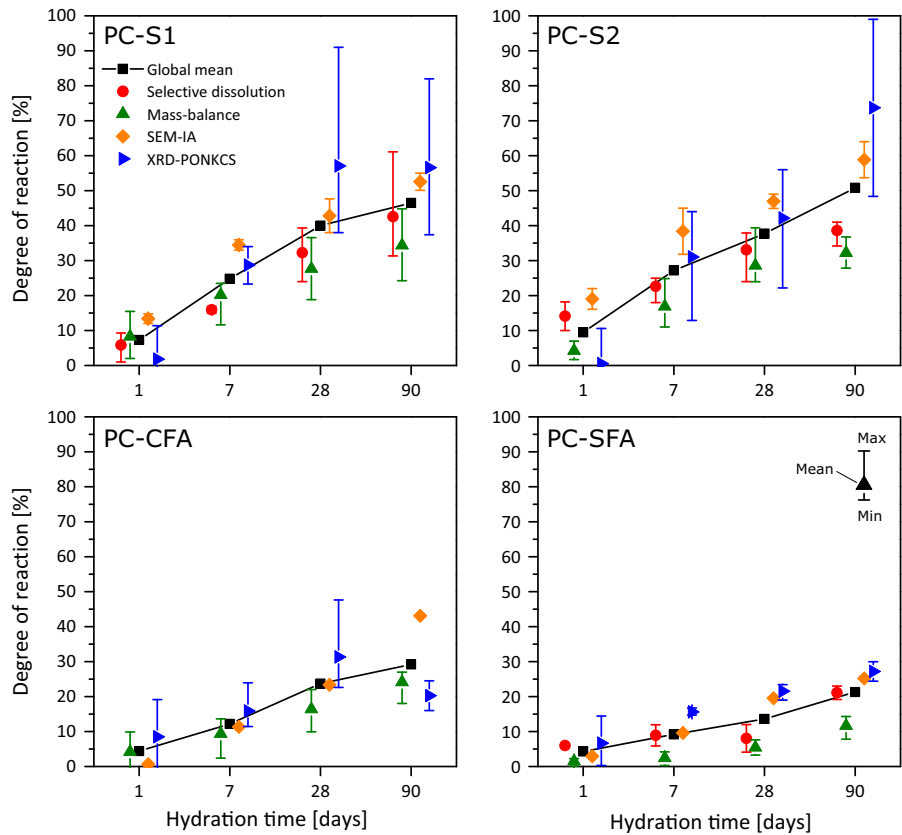


Fig. 3 Standard deviation of the determination of the degree of reaction of SCM using the techniques studied. Whiskers show the 90% confidence interval of determination of standard deviation. This interval depends on the amount of data available for each technique

for the different techniques as demonstrated by the whiskers. The upper and lower confidence bounds are calculated from the Chi squared distribution.

Figure 3 shows that generally the precision of determination of the degree of reaction using the techniques studied is rather low, at best $\pm 4\text{--}5\%$. This magnitude of uncertainty means that at one day of reaction the error may be similar to the measured degree of reaction of some SCMs and thus too large to allow comparison. Valid comparison can thus only be carried out from 7 days on, when the signal to noise ratio becomes acceptable.

Based on the data collected and the analysis of the combined inherent and inter-laboratory scatter, the most promising techniques are the electron microscopy, the selective dissolution using salicylic acid + HCl for siliceous ashes and the analysis of portlandite consumption. Selective dissolution of slags with EDTA + TEA + DEA was less reliable followed by PONKCS, whose scatter was the most pronounced.

5.2 Selective dissolution

Selective dissolution based on EDTA as a technique to determine the degree of reaction of slag has received



significant criticism [1], mostly regarding an incomplete correction procedure of the dissolved part of slag and the undissolved aluminosilicate hydrates. In this study the results were corrected for the part of slag dissolved, although as pointed out in [1] this correction may only be valid for early hydration ages. This is because the EDTA-soluble part of slag is expected to be the most reactive in paste. The undissolved aluminosilicate hydrates were not taken into account, which most likely resulted in underestimation of the results.

The selective dissolution technique based on salicylic acid + HCl could not be applied to the calcareous fly ash due to its significant solubility in the acid mixture (20–30 wt%). Nevertheless, the results obtained for the siliceous fly ash (0.5–2.0 wt% soluble) seem to agree quite well with the other techniques. As only two laboratories reported on this method, it is not yet possible to make conclusive judgements on the precision of this approach. Certainly, more comparative data are needed.

5.3 Consumption of portlandite analysed by mass-balance

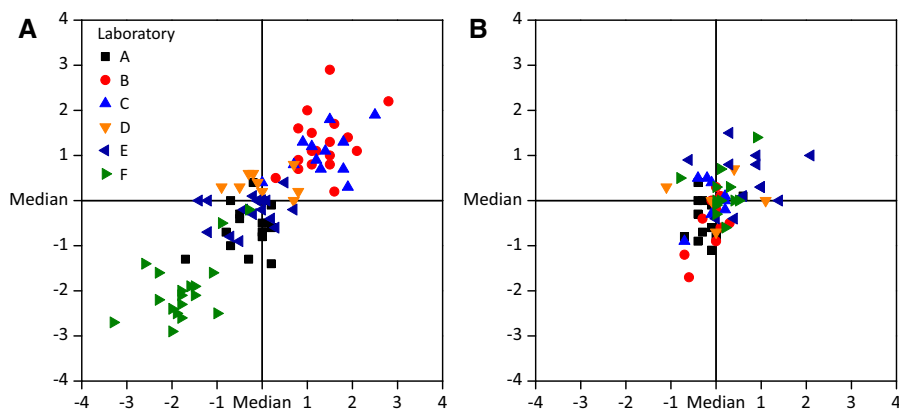
One of the main sources of scatter in the results of this technique is the scatter in portlandite content measured. As reported in [1], because the reaction of slags and calcareous fly ashes consumes little portlandite, a measurement error of ± 2 g portlandite/100 g anhydrous binder can lead to a relative change in the degree of SCM reaction of around 50%. Thanks to data available from several laboratories, we assess the uncertainty of determination of portlandite consumption to separate the inter-laboratory variation from the

inherent precision of the thermogravimetric technique. Figure 4 shows a statistical analysis of the results of portlandite content measured by the different laboratories using a modified Youden plot. A full description of construction and interpretation of Youden plots is given in [15]. To prepare Fig. 4a:

- Compute the median of the absolute portlandite content for each mix and age.
- Compute the difference between each single measurement and its corresponding median.
- Assign randomly the computed differences as X or Y coordinate and plot the points. The number of points in the plot is half the number of measurements, with each point representing two measurements according to their distance from the median, one shown in the X direction and the other in the Y direction.

Such construction clearly shows that in the absolute portlandite content measured, the most important difference results from an inter-laboratory bias and more specifically the way the tangential method is applied to quantify the mass loss due to portlandite dehydroxylation. However, the bias in data treatment is cancelled when differences of portlandite content are plotted instead of absolute values, in Fig. 4b. The scatter in this figure is about ± 1.5 g/100 g of anhydrous binder, which demonstrates the accuracy of the TGA and was roughly similar for all the participant laboratories. This scatter corresponds to a maximum relative error in degree of reaction of roughly 40%; in absolute terms, for example, $\pm 10\%$ for a degree of reaction of slag estimated at 25%. The corresponding confidence bounds in Fig. 2 are, however, much less, which is likely because the maximum positive and

Fig. 4 Modified Youden plots showing scatter of the thermogravimetric results (g/100 g of anhydrous binder) around their median values: **a** absolute portlandite content, **b** difference in portlandite between PC-SCM and PC-Q reference



negative error were not recorded for the same mix and age.

A serious drawback of the calculation of SCM reaction by mass balance of portlandite consumption is that it neglects the calcium provided to the pozzolanic reaction from the C–S–H formed from clinker reaction. The decreasing Ca/Si ratios of the C–S–H measured in the presence of SCMs in Table 4 and in the literature e.g. [3, 16] show that the reaction of the SCMs not only forms new C–S–H with lower Ca/Si ratio, but also takes Ca from the existing C–S–H. This means that the consumption of portlandite observed corresponds to much more SCM reaction than it would if no calcium was provided from the C–S–H. Thus, it should not be surprising that the results obtained by analysis of portlandite consumption in Fig. 2 all fall below the global average, regardless of the SCM tested.

To account for the calcium provided from existing C–S–H it is necessary to measure the masses of C_3S and C_2S reacted in the blended cement. One of the participant laboratories of this study carried out this measurement using X-ray powder diffraction with Rietveld refinement. These masses were converted to moles, the sum of which is equal to the number of moles of C–S–H formed. The Ca/Si ratio of this C–S–H was assumed to be 1.85, the same as in the fly ash systems at 1 day hydration and similar to what can be observed in plain Portland cement pastes [17]. The amount of calcium provided to the SCM reaction was then calculated as a difference between this Ca/Si ratio and that measured in Table 4. The degrees of reaction of the SCMs obtained in the aforementioned laboratory before and after correction are shown in Fig. 5. Although the mean does not take into account the updated values, it can be clearly seen that the correction delivers more realistic values. In PC-CFA the value at 90 days seems much overestimated though. This overestimation, especially at later ages, may be due to Ca being incorporated in AFm and Aft phases, which is not taken into account here.

Accounting for the Ca provided from existing C–S–H makes the calculated values sensitive to the measured Ca/Si ratios of the C–S–H, and this sensitivity increases with the Ca content of the SCM. In the extreme case of S1 and S2, the change of Ca/Si ratio by ± 0.05 would result in a change in the degree of reaction of around $\pm 15\%$ to $\pm 30\%$ absolute.

From the above data, it is clear that this seemingly straightforward technique actually requires much more effort than a mere measurement of the portlandite consumption, to give accurate results. Electron microscopy has to be carried out to measure the evolution of the Ca/Si ratio of the C–S–H and XRD-Rietveld analysis is required to estimate the amount of C–S–H formed from the reaction of clinker. The portlandite content could alternatively be measured by XRD-Rietveld instead of thermogravimetry.

5.4 SEM-image analysis

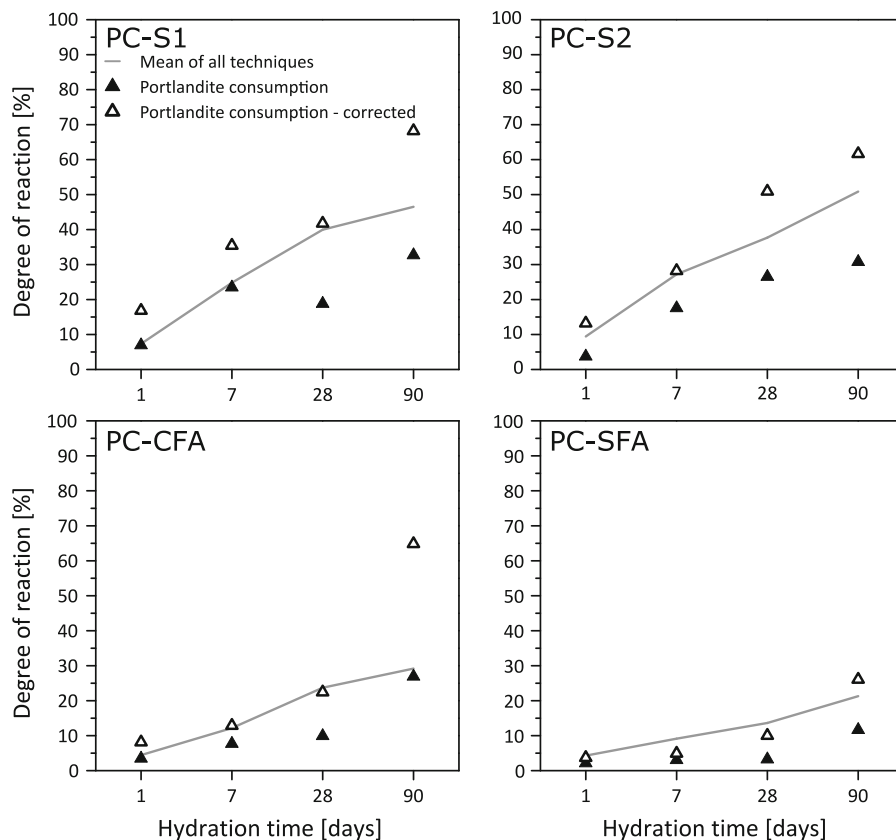
SEM-IA based on the segmentation of BSE grey levels was able to quantify the reaction of slags, and that based on the segmentation of EDS full element maps according to [4] could measure the reaction of both the slags and the fly ashes. An SEM-IA of EDS full element maps has a further advantage of being able to resolve the reaction of different types of glass present in fly ash, which is impossible using the other methods.

Compared to the results of the other techniques in Fig. 2 the SEM-IA tends to overestimate the degrees of hydration of S2, and those of S1 at early ages and CFA at 90 days. This is due to general drawbacks of microscopy: problems resolving fine particles, and because random cross-sections of 3-dimensional features are equal to or smaller than their actual equatorial cross-sections. Further, SEM analysis is much less available and it requires significantly more time and resources than the other techniques. Collection of a representative array of BSE images for a single sample and hydration time can take up to around 2 h. Eight EDS high quality full element maps take around 4 h to measure with a modern fast detector, while this type of data collection is far more time-consuming with older or benchtop instruments. Preparation of flat-polished sections can take several days and good polishing is essential to successful SEM analysis.

5.5 XRD-PONKCS

Among the techniques studied, by far the largest variations were observed for the XRD-PONKCS. For PC-SFA the results of the different laboratories were much more comparable, most likely due to less overlap between the “humps” of SFA and C–S–H,

Fig. 5 Degrees of reaction measured in one laboratory using the analysis of portlandite consumption before and after a correction, which estimates and takes into account the calcium provided to the reaction of the SCM by existing C–S–H



but also because the degrees of reaction were lower. Some of the PONKCS results should perhaps have been discarded as nonsense outliers. It is clear that at the present state of development this technique cannot give reproducible results between laboratories due to different refinement techniques.

Contrary to the other techniques studied, there is no strict protocol for how PONKCS model phases should be prepared and refined. The correct definition of the background is difficult, limiting the number of refined background parameters could improve the consistency of the results. Nevertheless, the major problem seems to be the overlap of the SCM contribution with that of the C–S–H, which is particularly important for slags. Indeed, in Fig. 2 the variation of the PONKCS results was higher for slag mixes and increased with hydration time, which was consistent with the higher expected error due to more C–S–H and less slag at higher hydration degrees. Published literature shows promising results of the PONKCS method applied to synthetic mixes of SCMs and C–S–H [7], but it now

seems that tackling real systems is more problematic. This problem may be even more important for low SCM replacement levels. In the synthetic systems, for slag amounts below 10 wt% at any hydration time the expected error was 2–3 wt% and for the amounts below 5 wt% the quantification was no longer valid. For an initial slag content of 30 wt% and 65% reaction after 90 days the remaining slag content would be around 10 wt% and the expected 3 wt% error would translate to a variation in the degree of reaction of 10%. In real systems, these values are expected to be much larger.

The decreased degree of reaction in PC-CFA after 90 days observed in Fig. 2 may be due to another issue. The model of an amorphous SCM phase used for PONKCS analysis is prepared on an anhydrous SCM. However, fly ashes and in particular the calcareous ones may be composed of a variety of glasses reacting at different rates [4]. This difference in reaction would affect the shape of the amorphous background in XRD over the course of the reaction and lead to errors.

6 Conclusions

This study examined four techniques: selective dissolution, analysis of the consumption of portlandite, SEM-image analysis and XRD-PONKCS to determine the degree of reaction of two slags, a calcareous and a siliceous fly ash in cement paste.

The results gathered show that the overall precision of the determination of the degree of reaction of SCMs in cement is rather low and varies depending on the technique used. The most precise, electron microscopy, selective dissolution of siliceous ash with salicylic acid + HCl and analysis of portlandite consumption, offered at best an absolute uncertainty around $\pm 5\%$. In terms of accuracy, the techniques were inspected for causes of potential under-/over-estimation of the degrees of reaction of SCMs.

Selective dissolution of slag cement pastes based on EDTA + TEA + DEA slightly underestimated the results compared to the other techniques, which is most likely due to failure to properly correct for the imperfections of the selectiveness of the dissolution. The analysis of siliceous fly ash cement pastes using salicylic acid + HCl seems to work fairly well, while it failed completely for the calcareous fly ash due to the high solubility of the anhydrous fly ash in the acid mixture.

Analysis of portlandite consumption was the most frequently reported technique. The inherent uncertainty of determination of the portlandite content by thermogravimetry of around ± 1.5 g/100 g of anhydrous binder leads to a scatter in the degree of reaction of roughly $\pm 5\%$ absolute. To avoid systematic and significant underestimations from the analysis of portlandite consumption analysis, it is necessary to make a more complete mass balance calculation, taking into account the decreasing Ca/Si ratio of the C–S–H in the presence of reacting SCMs and the fact that calcium is provided to the reaction not only by portlandite but also by the C–S–H formed previously in the reaction. With these factors accounted for the degrees of reaction seem more realistic, but the complete approach requires additional XRD and SEM measurements and remains sensitive to the Ca/Si ratio of the C–S–H.

BSE grey level analysis was used for slag cement pastes and that based on EDS full element maps successfully quantified the reaction of all the SCMs studied, including calcareous fly ash. SEM may overestimate the degrees of hydration due to the problem of resolving fine particles. SEM analysis requires more time and resources than the other techniques and it may be difficult to collect sufficient data with small desktop SEMs.

Compared to previous promising results on anhydrous systems, PONKCS appeared as a rather low-precision technique for the determination of degree of reaction of amorphous SCMs in hydrating cement pastes. So far, the only acceptable results were obtained for the siliceous fly ash cement paste. In terms of accuracy, however, the mean values of the PONKCS analysis tend to match fairly well with the mean results of the other techniques, notably for slag cements. This technique turns out to depend strongly on the expertise of the analyst and cannot be used as standard technique unless an improved, and more complete protocol is prepared and validated. The key issue seems to be the overlap between the contributions to amorphous background from the SCM and the C–S–H. If these two contributions cannot be reproducibly resolved, the use of PONKCS would have to be limited to materials not presenting this overlap.

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Compliance with ethical standards

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

Appendix: Experimental setups

See Tables 6, 7, 8, 9.



Table 6 Experimental setup for the thermogravimetric experiments

	Instrument	Sample mass (mg)	Temperature range (°C)	Heating rate (°C/min)	Gas, flow (mL/min)
A	Mettler Toledo TGA/SDTA 851e	20	40–980	20	N ₂ , 30
B	Mettler Toledo TGA/SDTA 851e	50	30–950	10	N ₂ , 30
C	Netzsch STA F449F3	30	30–1050	20	N ₂ , 20
D	Mettler Toledo TGA/DSC1, STAR ^o	50	25–900	10	N ₂ , 50
E	Netzsch STA 449F3	50	20–1100	10	N ₂ , 50
F	Perkin Elmer TGA 4000	20	30–1000	10	N ₂ , 40

The crucibles wait for the measurement covered with Al lids. The lid is removed prior to heating

Table 7 Experimental setup for electron microscopy and image analysis

	Instrument	kV	Analysed area	Signal	Noise filter
B	FEI Quanta 200 Bruker XFlash 4030 EDS	15	225 × 252 × 189 μm 8 × 252 × 189 μm	BSE + Mg, HQ full element maps	Hamming 25 px Hamming 7 px
E	ESEM XL-30 Philips	15	15 × 275 × 205 μm	BSE + Mg, Ca, Si	Median 2 × 2

Table 8 Experimental setup for powder XRD measurements

	Instrument	Sample loading	Standard	Source	Angles/step °2θ (CuKα)	Time per step	Slits
A	PANalytical X'Pert Pro MPD diffractometer + X'Celerator detector	Back	Internal 20 wt% TiO ₂	45 kV 40 mA incident beam CuK _{α1} monochromator	5–70/0.017	57.15 s cumulated	Divergence 0.5° anti-scatter 1°
B	PANalytical X'Pert Pro MPD diffractometer + X'Celerator detector	Back	External TiO ₂	45 kV 40 mA	6–70/0.017	59.69 s cumulated	Divergence 0.25°
C	Bruker D8 Advance + LynxEye silicon strip detector	Front	External NIST Cr ₂ O ₃	40 kV 40 mA	5–71/0.02	62 s cumulated	Divergence 0.3° soller 4°
E	Thermo Scientific ARL X'tra diffractometer + Peltier cooled detector	Side	Internal 10 wt% ZnO	40 kV 30 mA	5–70/0.02	1 s	Source L 1.30/ R 2.12 Receiver L 0.90/R 0.30

Table 9 Conditions of the XRD-Rietveld refinement with POKCS analysis

	A	B	C	E
Software	X'Pert HighScore Plus 4.1	X'Pert HighScore Plus 4.1	Topas V4.2	Topas Academic V4.1
Refined parameters				
Zero shift	×	×	×	×
Background	Chebyshev 1st order and 1/X parameter	Chebyshev 1st order and 1/X parameter	Chebyshev 3rd order	Chebyshev 12 polynomial terms



Table 9 continued

	A	B	C	E
Phase scale factors	×	×	×	×
Unit cell parameters	Up to 1% variation	Up to 1% variation	x	Up to 1% variation
Lorentzian peak broadening	×	×	×	×
Amorphous phase models				
Slag	HKL file	HKL file (P-42 m)	HKL file (Ia-3d)	A pseudo-Voigt peak
<i>Calibrated on/ Refined on</i>	<i>anhydrous PC-S2 mix</i>	<i>anhydrous slag</i>	<i>anhydrous slag</i>	<i>anhydrous slag</i>
Fly ash	n. a.	HKL file (P-1)	HKL file (Ima2)	A pseudo-Voigt peak
<i>Calibrated on/ Refined on</i>		<i>anhydrous fly ash</i>	<i>anhydrous fly ash</i>	<i>anhydrous fly ash</i>
C–S–H	HKL file based on a synthetic C–S–H with Ca/Si ratio of 1.6	Tobermorite 14Å crystal structure [18]	HKL file based on a synthetic C–S–H	One main and two secondary pseudo-Voigt peaks
<i>Refined on</i>		<i>corresponding 90-day cured pastes</i>	<i>PC-Q paste samples</i>	<i>PC-Q paste samples</i>

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