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

Authors

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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. Selective dissolution produced rather scattered and slightly underestimated results due to imperfect corrections. 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 reliable. A lack of a strict protocol and excessive overlap of slag and C-S-H signals were the main reasons behind the considerable scatter of the XRD-PONKCS results. The generated data showed that the precision of determination of the degree of reaction of SCMs in cement is rather low and at best $\pm 5\%$.

Keywords: Supplementary Cementitious Materials, Selective dissolution, Thermogravimetry, XRD, SEM-image analysis

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 the 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 have recently been summarized by the abovementioned 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. Despite corrections, large, non-quantifiable, systematic errors may remain and lead to spread in results [1].

An analysis of the SCM reaction from the consumption of portlandite was studied by mass-balance [1]. The degree of reaction of an SCM is calculated from the stoichiometric amount of silica required from the SCM to react with the portlandite. The errors are mainly related to the fact that the Ca/Si ratio of the C-S-H changes in the presence of reacting SCMs and that the uncertainty of portlandite content measured may propagate to a significant variation in the degree of reaction.

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 paste and is thus used to calculate the degree of reaction. The critical issue lies in an accurate segmentation of the images. BSE grey level of the SCMs is often similar to that of the hydrates and supplementary information may be required from EDS maps of element content. Slags are rich in Mg, which facilitates their separation but more sophisticated selection thresholds are needed to segment fly ash, with calcareous fly ash being the most difficult to tackle [5]. Overestimation of the degree of reaction may be due to the presence of very 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 actual equatorial sections [6].

By coupling PONKCS [3] to the XRD-Rietveld analysis the 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 excellent accuracy (2-3 wt.%) and precision (around 1 wt.%) [4]. However, in real

79 blended systems partial or entire overlap of the SCM signal with that of the main amorphous hydrate C-
80 S-H may lead to significant errors [1].

81
82 Binary pastes of Portland cement with two slags, a calcareous and a siliceous fly ash were prepared by
83 the coordinating laboratory (EPFL) and sent out to other participants for analysis. As each participant
84 followed their own protocols, the analysis of the collective data gave an idea of the maximum inter-
85 laboratory variability in the results, which should be universally applicable. This study assesses the
86 accuracy, precision and feasibility of application of the four selected techniques to determine degree of
87 reaction of slag or fly ash in composite cements.

88 **2 Participants**

89 Seven laboratories participated in this round robin test:

- 90 • Laboratory of Construction Materials, EPFL, Switzerland
- 91 • HeidelbergCement Technology Center GmbH, Germany
- 92 • Department of Materials Science and Engineering, The University of Sheffield, UK
- 93 • Magnel Laboratory for Concrete Research, Ghent University, Belgium
- 94 • Laboratory for Concrete and Construction Chemistry, Empa, Switzerland
- 95 • Institute of Building Materials Research, RWTH Aachen University, Germany
- 96 • Eduardo Torroja Institute of Construction Science (IETcc-CSIC), Spain

97
98 The participants were given the freedom to choose the techniques to apply and to follow their own
99 protocols. The laboratories were assigned random letters A-G.

100 **3 Materials**

101 The materials used for the study were Portland cement (PC), two slags (S1 and S2), siliceous fly ash
102 (SFA), calcareous fly ash (CFA) and quartz (Q). The chemical composition and the phase composition
103 of the anhydrous materials are given in Table 1. The XRD-Rietveld refinement of clinker phases in
104 anhydrous PC was carried out on samples treated with salicylic acid/methanol (SAM) and with
105 KOH/sucrose. The two slags investigated were > 99% amorphous and of very similar chemical
106 composition. The particle size distributions of the anhydrous materials were measured by laser diffraction
107 in isopropanol suspensions (refractive index components: $n = 1.70$, $k = 0.1$, solvent 1.39) using
108 a Malvern MasterSizer S and are presented in Figure 1.

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	2.0	-	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 + Ca(OH) ₂	1.7	-	0.2
P ₂ O ₅	-	-	0.3	0.1	0.2	0.0	Anhydrite	1.8	-	4.6
Mn ₂ O ₃	-	-	-	0.1	0.1	-	Arcanite	-	-	2.1
LOI (1050°C)	-	-	1.1	-	0.8	0.2	Periclase	-	-	0.2
Sum	100.0	100.0	98.5	100.0	99.8	100	Amorphous	89.7	65.8	-

Figure 1. Particle size distributions determined by laser diffraction.

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 wt.% and 30 wt.% quartz inert filler (PC-Q40 and PC-Q30 respectively). The powders were mixed with water at a water/binder ratio 0.4 using a laboratory mixer at 1600 rpm. 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 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 by gentle grinding prior to testing an outer layer of material from the samples, as it may have carbonated during the transport and storage.

4 Methods

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

Selective dissolution was carried out in triplicate on anhydrous fly ashes and slags 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 only 70-80 wt.% of CFA remained undissolved, which makes it unacceptable for the determination of the degree of reaction by this method. The residue of slags was rather low, around 90 wt.%, but still acceptable.

Table 2. Residues after selective dissolution of the anhydrous materials and the Portland cement paste [wt.%].

Laboratory		D (RWTH)	E (Ghent)	F (Sheffield)
EDTA+TEA+DEA	Anhydrous cement	0.42	0.43 ± 0.13	0.10 ± 0.01
	PC paste	1.31	-	-
	S1	89.92	95.03 ± 0.14	92.20 ± 0.47
	S2	90.12	95.20 ± 0.73	92.20 ± 0.47
Salicylic acid + HCl	Anhydrous cement	1.18	0.92	-
	PC paste	0.96	0.82	-
	CFA	71.70	79.48 ± 0.54	-
	SFA	97.94	99.68 ± 0.25	-

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 100 °C and weighed. This

treatment dissolves sulfate-bearing phases like ettringite or monosulfate, which later precipitate as gypsum and dehydrate to bassanite during the drying of the residue [7]. The SO₃ 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 thermo-gravimetry (ignition loss at 600 °C):

$$m_{\text{per 100 g anhydrous binder}} = \frac{m_{\text{per 100 g paste}}}{(1 - m_{\text{H}_2\text{O bound}})} = \frac{m_{\text{per 100 g paste}}}{m_{\text{TG residue at 600}^\circ\text{C}}} \quad (1)$$

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

$$\alpha_{\text{fly ash}} = \frac{100fp - R_b(1 - bS_b) + R_{PC}(1 - f)(1 - bS_{PC})}{100fp} \cdot 100\% \quad (2)$$

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 SO₃ = 1.813.

S_b = Mass of SO₃ in PC-FA paste residue in g/100 g of anhydrous binder.

S_{PC} = Mass of SO₃ in PC paste residue in g/100 g of anhydrous binder.

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 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 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 100 °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 hour 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:

$$\alpha_{\text{slag}} = \frac{100fp - R_b + R_{PC}(1 - f)}{f(100p - hM_s)} \cdot 100\% \quad (3)$$

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.
 M_S = Mass fraction of MgO in the slag glass.

4.2 Consumption of portlandite measured by thermogravimetry (A, B, C, D, E, F)

A summary of the setups used by the participants for thermogravimetric experiments is given in Table 5 in 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 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 equation (1).

Part of the CO₂ 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, this correction was not made as 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 should 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 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 mole of Si reacted the number of moles of Ca needed from portlandite are equal to:

$$\left(\frac{Ca}{Si}\right)_{C-S-H} - \left(\frac{Ca}{Si}\right)_{SCM} \quad (4)$$

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

$$\alpha f \frac{w_{SiO_2, SCM}}{M_{SiO_2}} \quad (5)$$

α = Degree of reaction of SCM.

f = Mass fraction of SCM in initial dry blend, 0.3 for fly ash and 0.4 for slag.

$w_{SiO_2, SCM}$ = Mass fraction of silica in the reactive amorphous part 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 thermo-gravimetric measurement and taking into account for CFA the portlandite present in this ash and the portlandite that forms from the C_2S and free lime in it:

$$\frac{\Delta m_{CH}}{M_{CH}} - 100f \left(\frac{m_{CH \text{ in SCM}}}{M_{CH}} + \frac{m_{CaO \text{ in SCM}}}{M_{CaO}} + \frac{m_{C_2S \text{ in SCM}}}{M_{C_2S}} \left(2 - \left(\frac{Ca}{Si} \right)_{C-S-H} \right) \right) \quad (6)$$

Δm_{CH} = Difference in the mass of portlandite between PC-SCM and PC-Q30/Q40, expressed in g/100g anhydrous binder.

$m_{CH \text{ in SCM}}$ = Mass of portlandite in 100 g unreacted SCM.

$m_{Lime \text{ in SCM}}$ = Mass of free lime in 100 g unreacted SCM.

$m_{C_2S \text{ in SCM}}$ = Mass of C_2S 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_{C_2S} = Molar mass of C_2S = 172.24 g/mol.

The value of 2 in the above equation corresponds to the Ca/Si ratio of C_2S .

Since (4) $\times$ (5) = (6), the degree of reaction can be expressed as:

$$\alpha = \frac{\frac{\Delta m_{CH}}{M_{CH}} - 100f \left(\frac{m_{CH \text{ in SCM}}}{M_{CH}} + \frac{m_{Lime \text{ in SCM}}}{M_{CaO}} + \frac{m_{C_2S \text{ in SCM}}}{M_{C_2S}} \left(2 - \left(\frac{Ca}{Si} \right)_{C-S-H} \right) \right)}{f \frac{w_{SiO_2,SCM}}{M_{SiO_2}} \left(\left(\frac{Ca}{Si} \right)_{C-S-H} - \left(\frac{Ca}{Si} \right)_{SCM} \right)} \cdot 100\% \quad (7)$$

The $\left(\frac{Ca}{Si} \right)_{SCM}$ and $w_{SiO_2,SCM}$ were derived from the XRF bulk chemical composition data. A distinction was made between the reactive and the non-reactive part of the fly ashes studied. 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 0.897 for CFA and 0.658 for SFA. The $\left(\frac{Ca}{Si} \right)_{SCM}$ and the $w_{SiO_2,SCM}$ were calculated from the theoretical composition of this fraction.

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 [9–12] show that the Ca/Si ratio of the C-S-H in blended cements decreases with the reaction degree. However, this ratio cannot be simply taken from the published data. As shown in [12], the scatter of the Ca/Si ratios between mixes containing similar amounts of portlandite can vary in the range of ± 0.1 , which is too much. 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. [13] recently improved by Rossen and Scrivener [14]. The results are shown in Table 3. 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 around ± 0.05 . The resulting uncertainty on the degree of reaction was rather low and, depending on hydration time, ranged from $\pm 0.3\%$ to $\pm 2.6\%$ for slags, from $\pm 0.1\%$ to $\pm 0.4\%$ for SFA and from $\pm 0.2\%$ to $\pm 1.0\%$ for CFA.

The decreasing Ca/Si ratios in Table 3 indicate that besides the Ca from portlandite, a considerable amount of Ca comes from the C-S-H formed at earlier stages of reaction. A dedicated correction requires an additional measurement of the degree of reaction of C_3S and C_2S from the clinker and is discussed in Section 5.3. The potential consumption of Ca to form AFt/AFm phases was not accounted for.

Table 3. Ca/Si ratios of the C-S-H used for the calculation of the degree of reaction of SCMs from portlandite consumption. Uncertainty of determination was estimated at ± 0.05 .

	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

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 6. Unreacted slag was quantified using BSE images and EDS maps of Mg (lab B) or Mg, Ca, Si (lab E) similarly to [15]. Unreacted fly ash was segmented using high quality EDS maps of all main elements present, as in [5]. The degree of reaction of the SCMs was computed as:

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

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 6. Experimental setup for electron microscopy and image analysis.

	Instrument	kV	Analysed area	Signal	Noise filter
B	FEI Quanta 200	15	225 x 252x189 μm	BSE + Mg,	Hamming 25 px
	Bruker XFlash 4030 EDS		8 x 252x189 μm	HQ full element maps	Hamming 7 px
E	ESEM XL-30 Philips	15	15 x 275x205 μm	BSE + Mg, Ca, Si	Median 2x2

Table 7 in appendix. Rietveld refinement with PONKCS analysis was carried out under conditions specified in Table 8 in appendix. The results of the refinements were recalculated to g/100g anhydrous binder using equation (1).

5 Results and Discussion

The degrees of reaction of the four SCMs studied are given in Table 4 and Figure 2. In the latter 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.

Table 4. Degrees of reaction of SCMs [%] measured by the techniques investigated. Shaded 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.

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

Figure 2. Comparison of mean and min-max 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.

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 pooled standard deviation. First, a standard deviation was calculated for each technique and testing time. It was then found that the obtained values did not change significantly with time and were thus pooled to calculate the final result, which is shown in Figure 3. All calculations were carried out at 90 % confidence interval. This means that, for example, the uncertainty of determination of the degree of reaction of slag using EDTA-based selective dissolution is between $\pm 7\%$ and $\pm 15\%$ reaction for 90 % of the results and that the most likely uncertainty was $\pm 10\%$ absolute. The upper and lower bounds are different as they are only symmetric in log-normal space.

Figure 3. Standard deviation of the determination of the degree of reaction of SCM using the techniques studied shown together with its 90 % confidence interval.

Figure 3 shows that on the overall the precision of determination of the degree of reaction using the techniques studied is rather low, at best ± 4 -5 %. This magnitude of uncertainty means that at one day of reaction the error is in the range of the measured degree of reaction and thus too large to allow comparison of different SCMs. Valid comparison can only be carried out from 7 days on when the signal to noise ratio becomes acceptable.

In the view of the combined inherent and inter-laboratory scatter, the most promising techniques seem to be the analysis of portlandite consumption and the electron microscopy. Selective dissolution techniques appear as less reliable followed by PONKCS, whose scatter was the most pronounced. Because the protocols differed between the laboratories, the reported ranges are expected to be universally applicable to any laboratory following the procedures studied.

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 before 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 [16]. To

- 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.

Figure 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.

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 Figure 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, ± 10 % for a degree of reaction of slag estimated at 25 %, for example.

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. Decreasing Ca/Si ratios of the C-S-H measured in the presence of SCMs in Table 3 and in literature e.g. [9,17] 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 Figure 2 are somewhat underestimated 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, 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 [18]. 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 3. The degrees of reaction of the SCMs obtained in the aforementioned laboratory before and after correction are shown in Figure 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. Indeed, 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. The change of Ca/Si ratio by ± 0.015 would result in a change in the degree of reaction of around $\pm 5\%$ to $\pm 10\%$ absolute.

Figure 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.

From the above data, it is clear that this seemingly easy technique actually requires much more effort than a mere measurement of the portlandite consumption. 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 can be measured by XRD-Rietveld instead of thermo-gravimetry.

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 [5] 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 Figure 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 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 hours. Eight EDS high quality full element maps take around 4 hours 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, but also because the degrees of reaction were lower. Some of the PONKCS results should 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 of how PONKCS model phases should be prepared and refined. The correct definition of the background is difficult, but 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 Figure 2 the variation of the PONKCS results was higher for slag mixes and increased with hydration time, which seems to match with higher expected error due to more C-S-H and less slag at higher hydration degrees. Published literature showed promising results of the PONKCS method applied to synthetic mixes of SCMs and C-S-H [4], but it now seems that tackling real systems is much 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.

A decreased degree of reaction in PC-CFA after 90 days observed in Figure 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 [5]. 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 looked at 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 gathered results 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, analysis of portlandite consumption and electron microscopy, 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 likely due to incomplete correction procedures. 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 its high solubility in the acid mixture.

Portlandite consumption analysis was the most frequently reported technique. The inherent uncertainty of determination of the portlandite content by thermo-gravimetry 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 significant underestimations from the mass balance analysis, it is necessary to take 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 little desktop SEM may fail to collect sufficient data.

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 analyst expertise and cannot be used as standard technique unless an improved, careful and strict 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.

References

- [1] K.L. Scrivener, B. Lothenbach, N. De Belie, E. Gruyaert, J. Skibsted, R. Snellings, et al., TC 238-SCM: hydration and microstructure of concrete with SCMs, *Mater. Struct.* 48 (2015) 835–862.
- [2] I. Pane, W. Hansen, Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, *Cem. Concr. Res.* 35 (2005) 1155–1164.
- [3] N.V.Y. Scarlett, I.C. Madsen, Quantification of phases with partial or no known crystal structures, *Powder Diffr.* 21 (2006) 278–284.
- [4] R. Snellings, A. Salze, K.L. Scrivener, Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements, *Cem. Concr. Res.* 64 (2014) 89–98.
- [5] P.T. Durdziński, C.F. Dunant, M. Ben Haha, K.L. Scrivener, A new quantification method based on SEM-EDS to assess fly ash composition and study the reaction of its individual components in hydrating cement paste, *Cem. Concr. Res.* 73 (2015) 111–122.
- [6] K. Scrivener, Backscattered electron imaging of cementitious microstructures: Understanding and quantification, *Cem. Concr. Compos.* 26 (2004) 935–945.
- [7] A. Vollpracht, W. Brameshuber, Investigations on ten years old hardened cement paste samples, in: *Int. Rilem Conf. Mater. Sci.*, 2010: pp. 79–91.
- [8] J.S. Lumley, R.S. Gollop, G.K. Moir, H.F.W. Taylor, Degrees of reaction of the slag in some blends with Portland cements, *Cem. Concr. Res.* 26 (1996) 139–151.
- [9] F. Deschner, F. Winnefeld, B. Lothenbach, S. Seufert, P. Schwesig, S. Ditttrich, et al., Hydration of Portland cement with high replacement by siliceous fly ash, *Cem. Concr. Res.* 42 (2012) 1389–1400.
- [10] M. Whittaker, M. Zajac, M. Ben Haha, F. Bullerjahn, L. Black, The role of the alumina content of slag, plus the presence of additional sulfate on the hydration and microstructure of Portland

- cement-slag blends, *Cem. Concr. Res.* 66 (2014) 91–101.
- [11] J.E. Rossen, B. Lothenbach, K.L. Scrivener, Composition of C–S–H in pastes with increasing levels of silica fume addition, *Cem. Concr. Res.* 75 (2015) 14–22.
- [12] J.E. Rossen, B. Lothenbach, K.L. Scrivener, Composition of C–A–S–H in matured blended cement pastes, (In Preparation). (n.d.).
- [13] C. Famy, A.R. Brough, H.F.W. Taylor, The C–S–H gel of Portland cement mortars: Part I. The interpretation of energy-dispersive X-ray microanalyses from scanning electron microscopy, with some observations on C–S–H, AFm and Aft phase compositions, *Cem. Concr. Res.* 33 (2003) 1389–1398.
- [14] J.E. Rossen, K.L. Scrivener, Optimisation of SEM–EDS to determine C–S–H composition in matured cement paste samples, *Mater. Charact.* (n.d.).
- [15] V. Kocaba, E. Gallucci, K.L. Scrivener, Methods for determination of degree of reaction of slag in blended cement pastes, *Cem. Concr. Res.* 42 (2012) 511–525.
- [16] W.J. Youden, Graphical diagnosis of interlaboratory test results, *Ind. Qual. Control.* 15 (1959) 24–28.
- [17] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, *Cem. Concr. Res.* 41 (2011) 1244–1256.
- [18] H.F.W. Taylor, *Cement Chemistry*, 1997.
- [19] E. Bonaccorsi, S. Merlino, A.R. Kampf, The Crystal Structure of Tobermorite 14 Å (Plombierite), a C–S–H Phase, *J. Am. Ceram. Soc.* 88 (2005) 505–512.

Appendix1 – Experimental setups

Table 5. Experimental setup for the thermogravimetric experiments. In automated TGA experiments on open crucibles, the crucibles wait for the measurement covered with Al lids.

Instrument	Sample mass [mg]	Crucible	T range [°C]	Heating rate [°C/min]	Gas, flow [mL/min]
A Mettler Toledo TGA/SDTA 851e	20	open	40 - 980	20	N ₂ , 30
B Mettler Toledo TGA/SDTA 851e	50	open	30 - 950	10	N ₂ , 30
C Netzsch STA F449F3	30	open	30-1050	20	N ₂ , 20
D RWTH					
E Netzsch STA 449F3	50	open	20 - 1100	10	N ₂ , 50
F Perkin Elmer TGA 4000	20		30 - 1000	10	N ₂ , 40

Table 6. Experimental setup for electron microscopy and image analysis.

Instrument	kV	Analysed area	Signal	Noise filter
B FEI Quanta 200	15	225 x 252x189 µm	BSE + Mg,	Hamming 25 px
Bruker XFlash 4030 EDS		8 x 252x189 µm	HQ full element maps	Hamming 7 px
E ESEM XL-30 Philips	15	15 x 275x205 µm	BSE + Mg, Ca, Si	Median 2x2

561 Table 7. 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	57.15s 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	59.69s 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	62s 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	1s	Source L 1.30/R 2.12 Receiver L 0.90/R 0.30

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563 Table 8. Conditions of the XRD-Rietveld refinement with PONKCS 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	x	x	x	x
Background		Chebyshev 1 st order and 1/X parameter	Chebyshev 3 rd order	Chebyshev 12 polynomial terms
Phase scale factors		x	x	x
Unit cell parameters		Up to 1% variation	x	Up to 1% variation
Lorentzian peak broadening		x	x	x
Amorphous phase models				
Slag	HKL file	HKL file (P-42m)	HKL file (1a-3d)	A pseudo-Voigt peak
Calibrated on	anhydrous PC-S2 mix	anhydrous slag	anhydrous slag	
Fly ash	n. a.	HKL file (P-1)	HKL file (1ma2)	A pseudo-Voigt peak
Calibrated on		anhydrous fly ash	anhydrous fly ash	
C-S-H	HKL file based on a synthetic C-S-H with Ca/Si ratio of 1.6	Tobermorite 14Å crystal structure [19]	HKL file based on a synthetic C-S-H	One main and two secondary pseudo-Voigt peaks
Refined on		corresponding 90-day cured pastes	PC-Q paste samples	PC-Q paste samples

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