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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. 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

39 **1 Introduction**

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

51
52 Selective dissolution of composite cement pastes aims to dissolve all paste components except the
53 unreacted SCM, which can then be quantified. In practice, a part of the slag or fly ash is dissolved while
54 some hydrates and unreacted clinker remain. Despite corrections, large, non-quantifiable, systematic
55 errors may remain and lead to spread in results [1].

56
57 An analysis of the SCM reaction from the consumption of portlandite was studied by mass-balance [1].
58 The degree of reaction of an SCM is calculated from the stoichiometric amount of silica required from
59 the SCM to react with the portlandite. The errors are mainly related to the fact that the Ca/Si ratio of the
60 C-S-H changes in the presence of reacting SCMs and that the uncertainty of portlandite content measured
61 may propagate to a significant variation in the degree of reaction.

62
63 SEM-IA of epoxy impregnated polished sections uses backscatter electron images (BSE) and EDS maps
64 of the content of elements to extract areas in the images that correspond to anhydrous SCMs. The area
65 fraction of anhydrous SCMs in images is equal to their volume fraction in paste and is thus used to
66 calculate the degree of reaction. The critical issue lies in an accurate segmentation of the images. BSE
67 grey level of the SCMs is often similar to that of the hydrates and supplementary information may be
68 required from EDS maps of element content. Slags are rich in Mg, which facilitates their separation but
69 more sophisticated selection thresholds are needed to segment fly ash, with calcareous fly ash being the
70 most difficult to tackle [5]. Overestimation of the degree of reaction may be due to the presence of very
71 fine SCM particles, below or around the resolution of the microscope and because in images, the captured
72 sections of 3D features appear mostly smaller than the actual equatorial sections [6].

73
74 By coupling PONKCS [3] to the XRD-Rietveld analysis the different amorphous materials can be
75 quantified from their diffuse scattering 'hump'. A separate scan of the amorphous component is used to
76 calibrate a model, which relates the diffraction signal of this component to its content. An assessment of
77 this relatively new technique to quantify SCMs in model mixes of slag, metakaolin, quartz and hydrated
78 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**

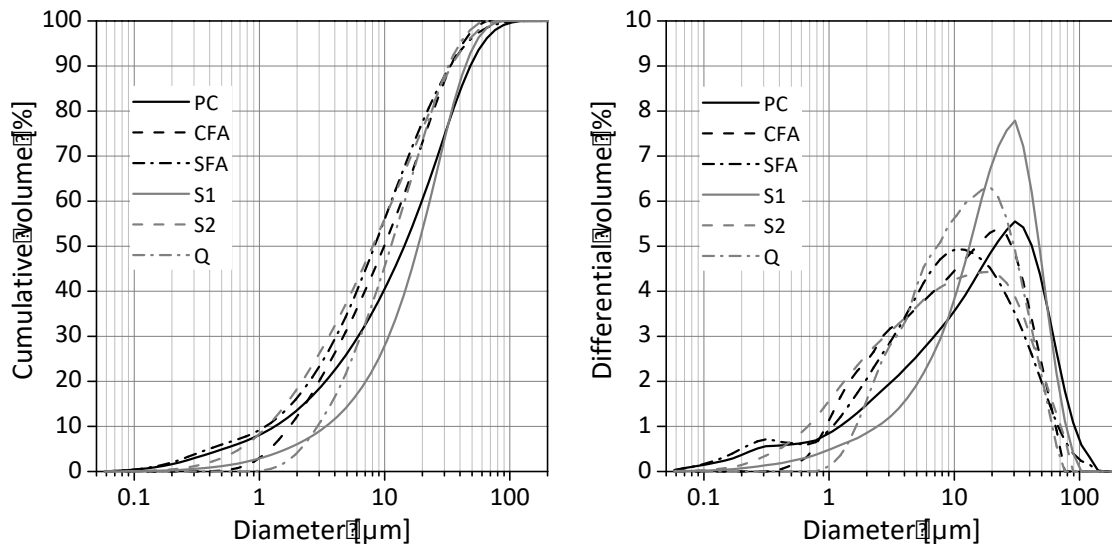
101 The materials used for the study were Portland cement (PC), two slags (S1 and S2), siliceous fly ash
102 (SFA), calcareous fly ash (CFA) and quartz (Q). The chemical composition and the phase composition
103 of the anhydrous materials are given in Table 1. The XRD-Rietveld refinement of clinker phases 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.

109

110 Table 1. Bulk chemical composition by X-ray fluorescence and phase composition by XRD-Rietveld
 111 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	-

112



113

114 Figure 1. Particle size distributions determined by laser diffraction.

115

116 The study was carried out using paste samples, all of which were prepared by one laboratory. Binary
 117 composite cements were prepared with PC and 40 wt.% slag (PC-S1 and PC-S2) or 30 wt.% fly ash (PC-
 118 SFA and PC-CFA). Reference samples included neat PC and mixes of PC with 40 wt.% and 30 wt.%
 119 quartz inert filler (PC-Q40 and PC-Q30 respectively). The powders were mixed with water at
 120 a water/binder ratio 0.4 using a laboratory mixer at 1600 rpm. The pastes were cast in cylindrical
 121 polypropylene containers of 33 mm internal diameter and sealed-cured for 1, 7, 28 and 90 days.
 122 Additional samples were demoulded after 1 day and water-cured until 28 and 90 days in slightly larger

123 containers topped with a minimal amount of water. After curing, discs of around 2-3 mm thickness and
 124 33 mm diameter were cut from the paste cylinders. These discs were stored in lots of six per 200 mL of
 125 isopropanol for 7 days to stop hydration by solvent exchange. The isopropanol was replaced after 1 and
 126 3 days of storage. The discs were then kept in vacuum desiccators (approx. 7 mbar) for 7 days to remove
 127 the isopropanol. After that, the samples were sealed in vacuum bags and sent out to the participants. The
 128 participants removed by gentle grinding prior to testing an outer layer of material from the samples, as it
 129 may have carbonated during the transport and storage.

130 4 Methods

131 4.1 Selective dissolution of fly ash cement pastes with salicylic acid + HCl (D,E) and of slag cement 132 pastes with EDTA + TEA + DEA (D, E, F, G)

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

136

137 The dissolution of anhydrous cement, slags, fly ashes and the neat PC paste was carried out to determine
 138 the undissolved residue of these materials, which in the perfect case should be zero for the Portland
 139 cement and its paste and 100 wt.% for the SCMs. Details of the dissolution procedures are provided in
 140 further parts of this section. The results given in Table 2 show that only 70-80 wt.% of CFA remained
 141 undissolved, which makes it unacceptable for the determination of the degree of reaction by this method.
 142 The residue of slags was rather low, around 90 wt.%, but still acceptable.

143

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

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

146

147 Unreacted fly ashes and PC-fly ash pastes in 2 ± 0.02 g samples were mixed for 30 min with 200 mL
 148 of HCl + salicylic acid + methanol, a method based on the European standard CEN/TR 196-4 (2007) for
 149 the determination of the composition of anhydrous blended cements. The acid solution was prepared
 150 from 41 mL HCl and 50 mg salicylic acid, made up to 1000 mL with methanol. The dissolution residues
 151 were vacuum filtrated on pre-dried glass fibre filters, washed, dried at 100 $^{\circ}\text{C}$ and weighed. This

152 treatment dissolves sulfate-bearing phases like ettringite or monosulfate, which later precipitate as
 153 gypsum and dehydrate to bassanite during the drying of the residue [7]. The SO₃ content in the residue
 154 needed for the sulfate correction was determined by the combustion infrared detection technique. Values
 155 expressed per 100 g of isopropanol-vacuum dried paste were converted to per 100 g of anhydrous binder
 156 basis using bound water content measured by thermo-gravimetry (ignition loss at 600 °C):

157

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

158

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

160

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

161

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

163 p = Mass fraction of fly ash undissolved by salicylic acid + HCl.

164 R_b = Mass of residue from the PC-FA paste in g/100 g anhydrous binder.

165 R_{PC} = Mass of residue from the PC paste in g/100 g anhydrous binder.

166 b = Mass of bassanite formed from 1 g of SO₃ = 1.813.

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

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

169

170 Unreacted slag and PC-S paste triplicate samples were subjected to EDTA-TEA-DEA attack. Based on
 171 the procedure described by Lumley *et al.* [8], 93.0 g of disodium EDTA + 250 mL of TEA + 500 mL of
 172 water + 173 mL of DEA were mixed and made up to 1000 mL with water. For each extraction test, 50 mL
 173 of the above solution was diluted to approximately 800 mL with water and brought to a temperature of
 174 20.0 ± 2 °C. Then 0.50 ± 0.02 g of dried and ground sample paste was weighed to the nearest 0.0001 g
 175 and sprinkled over the surface of solution. The mixture of the solution and the ground sample was stirred
 176 for 120 ± 5 min at the stated temperature. In laboratories D and E the dissolution residues were vacuum
 177 filtrated on pre-dried glass fibre filters, washed, dried at 100 °C and weighed. In laboratory F the residues
 178 were filtered under vacuum through a 90 mm diameter Whatman GF/C filter. This filter had been
 179 previously washed with 100 mL of distilled water, dried at 105 °C and weighed. The residue was washed
 180 5 times with 10 mL lots of distilled water, dried at 105 °C for 1 hour and weighed to the nearest 0.0001 g.
 181 The residues contained unreacted slag and undissolved hydrates, in particular hydrotalcite-like phases,
 182 which were accounted for as in [8] and the degree of reaction of slag α was computed as:

183

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

184

185 f = Mass fraction of slag in initial dry blend = 0.4.

186 p = Mass fraction of slag undissolved by EDTA.

- 187 R_b = Mass of residue from the PC-S paste in g/100 g of anhydrous binder.
 188 R_{PC} = Mass of residue from the PC paste in g/100 g of anhydrous binder.
 189 h = Mass of dried hydrotalcite formed from 1 g of MgO in the slag glass = 2.35.
 190 M_S = Mass fraction of MgO in the slag glass.

191 4.2 Consumption of portlandite measured by thermogravimetry (A, B, C, D, E, F)

192 A summary of the setups used by the participants for thermogravimetric experiments is given in Table 5
 193 in appendix. In TG curves the mass loss around 450°C was assigned to water from the dehydroxylation
 194 of portlandite. Because of the non-zero background mainly due to water lost from C-S-H the mass loss
 195 from portlandite could not be quantified by a simple horizontal step. A tangential technique was used in
 196 two variants: (1) a tangential step, in which the mass difference is calculated at the inflection point of the
 197 DTG peak (A, D, F), and (2) a tangential step between the onset and the end of the DTG peak (B, C, E).
 198 The amount of portlandite was computed by multiplying the obtained mass loss by the ratio of molar
 199 mass of portlandite and of water = 74.09/18.02 and was expressed per 100 g of anhydrous binder using
 200 equation (1).

201

202 Part of the CO₂ emitted during heating may come from carbonated portlandite, the amount of which can
 203 be calculated and added to the amount of portlandite quantified from the water loss. In this study, this
 204 correction was not made as the samples had been treated with isopropanol, which may also contribute to
 205 the CO₂ emitted and thus result in errors.

206

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

211

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

215

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

216

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

218

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

219

220 α = Degree of reaction of SCM.

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

222 $w_{SiO_2,SCM}$ = Mass fraction of silica in the reactive amorphous part of the SCM.

223 M_{SiO_2} = Molar mass of silica = 60.08 g/mol.

224

225 The absolute number of moles of portlandite consumed by the SCM reaction is calculated from the
226 thermo-gravimetric measurement and taking into account for CFA the portlandite present in this ash and
227 the portlandite that forms from the C_2S and free lime in it:

228

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

229

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

232 $m_{CH \text{ in SCM}}$ = Mass of portlandite in 100 g unreacted SCM.

233 $m_{Lime \text{ in SCM}}$ = Mass of free lime in 100 g unreacted SCM.

234 $m_{C_2S \text{ in SCM}}$ = Mass of C_2S in 100 g unreacted SCM.

235 M_{CH} = Molar mass of portlandite = 74.09 g/mol.

236 M_{CaO} = Molar mass of CaO = 56.08 g/mol.

237 M_{C_2S} = Molar mass of C_2S = 172.24 g/mol.

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

239

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

241

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

242

243 The $\left(\frac{Ca}{Si} \right)_{SCM}$ and $w_{SiO_2, SCM}$ were derived from the XRF bulk chemical composition data. A distinction
244 was made between the reactive and the non-reactive part of the fly ashes studied. The theoretical
245 composition of the reactive amorphous part was computed by subtracting from the bulk chemical
246 composition the amounts of oxides corresponding to crystalline phases (Table 1). The reactive
247 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
248 calculated from the theoretical composition of this fraction.

249

250 For the calculation of the degree of reaction of SCMs from the portlandite consumption it is necessary
251 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
252 blended cements decreases with the reaction degree. However, this ratio cannot be simply taken from the
253 published data. As shown in [12], the scatter of the Ca/Si ratios between mixes containing similar
254 amounts of portlandite can vary in the range of ± 0.1 , which is too much. Thus, in this study the chemical
255 composition of the C-S-H was measured by one of the laboratories following the SEM-EDS point

256 analysis procedure of Famy *et al.* [13] recently improved by Rossen and Scrivener [14]. The results are
 257 shown in Table 3. It was difficult to obtain reliable data at 1 day of hydration, hence the Ca/Si ratios at
 258 7-day hydration were also used for the analysis of the 1-day samples. The uncertainty of determination
 259 of Ca/Si ratio of the C-S-H using this technique was estimated around ± 0.05 . The resulting uncertainty
 260 on the degree of reaction was rather low and, depending on hydration time, ranged from $\pm 0.3\%$ to \pm
 261 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.

262

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

267

268 Table 3. Ca/Si ratios of the C-S-H used for the calculation of the degree of reaction of SCMs from
 269 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

270

271 4.3 SEM-image analysis (B, E)

272 Polished sections of epoxy-impregnated paste discs were coated with ~ 15 nm of conductive carbon and
 273 analysed using SEM - image analysis. Details of the setups are given in the appendix Table 6. Unreacted
 274 slag was quantified using BSE images and EDS maps of Mg (lab B) or Mg, Ca, Si (lab E) similarly to
 275 [15]. Unreacted fly ash was segmented using high quality EDS maps of all main elements present, as in
 276 [5]. The degree of reaction of the SCMs was computed as:

277

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

278

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

280 4.4 XRD-PONKCS (A, B, C, E)

281 X-ray powder diffraction measurements were carried out on anhydrous SCMs and on ground pastes using
 282 the experimental setups summarized in Table 6. Experimental setup for electron microscopy and image
 283 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

284

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

288 5 Results and Discussion

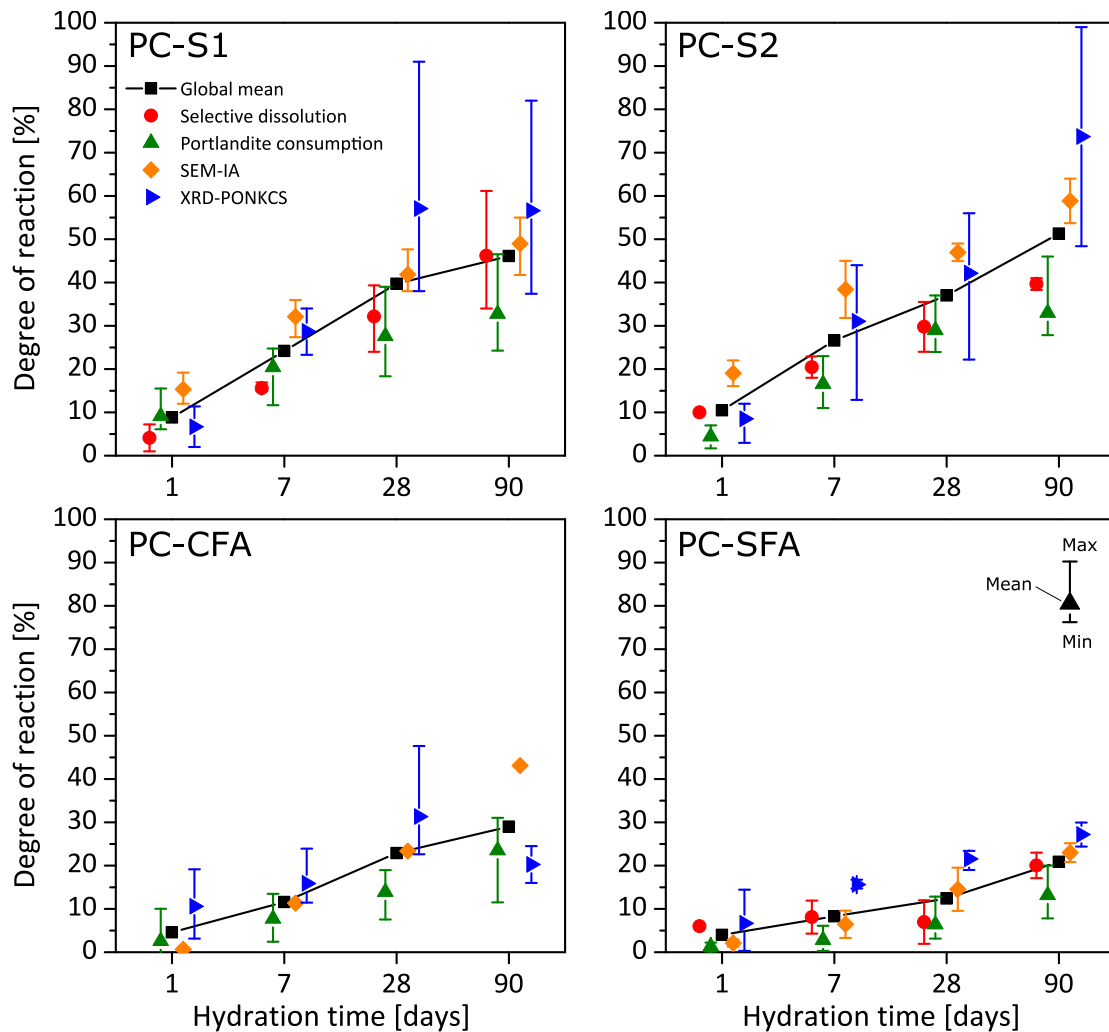
289 The degrees of reaction of the four SCMs studied are given in Table 4 and Figure 2. In the latter the
 290 points correspond to the mean degree of reaction and the whiskers show min-max values. A global mean
 291 was calculated as an average of means.

292

293 Table 4. Degrees of reaction of SCMs [%] measured by the techniques investigated. Shaded columns
 294 correspond to water-cured samples. Selective dissolution of slags was based on EDTA + TEA + DEA
 295 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							
Selective dissolution	D		15	33	43				23	36	38					4	2	17								
	E	1	15	24	34	29	40	10	18	24	41	26	38	Not reliable, CFA too soluble in the acid mixture				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	

296



297

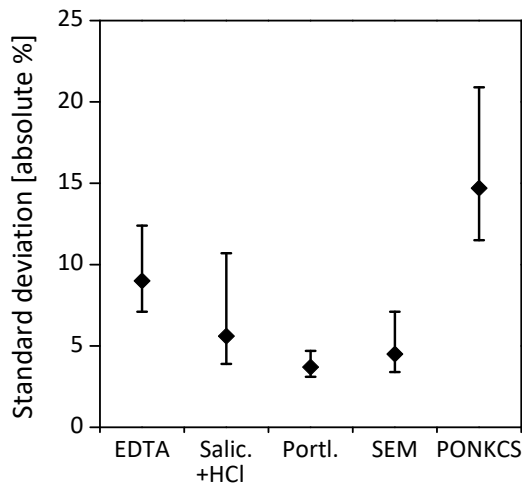
298 Figure 2. Comparison of mean and min-max degrees of SCM reaction measured. Selective dissolution
 299 did not work for the calcareous fly ash (PC-CFA) and for this material only one series of SEM-IA results
 300 was reported. The results for water-cured samples are not shown.

301 *5.1 Precision and accuracy of the techniques studied*

302 Precision of a technique comprises the uncertainty of measurement due to the technique itself and due to
 303 the inter-laboratory scatter. Accuracy, on the other hand, demonstrates how far the results are shifted
 304 from the actual degree of reaction. Because the actual degree of hydration of the SCMs remains unknown,
 305 the accuracy can only be assessed by a comparison to the global mean and by analysing potential causes
 306 of under-/over-estimated results. This will be discussed for each technique separately in further sections.
 307

308 In this section the precision is assessed using pooled standard deviation. First, a standard deviation was
 309 calculated for each technique and testing time. It was then found that the obtained values did not change
 310 significantly with time and were thus pooled to calculate the final result, which is shown in Figure 3. All
 311 calculations were carried out at 90 % confidence interval. This means that, for example, the uncertainty
 312 of determination of the degree of reaction of slag using EDTA-based selective dissolution is between \pm
 313 7 % and \pm 15 % reaction for 90 % of the results and that the most likely uncertainty was \pm 10 % absolute.
 314 The upper and lower bounds are different as they are only symmetric in log-normal space.

315



316

317 Figure 3. Standard deviation of the determination of the degree of reaction of SCM using the techniques
318 studied shown together with its 90 % confidence interval.
319

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

325

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

331 5.2 Selective dissolution

332 Selective dissolution based on EDTA as a technique to determine the degree of reaction of slag has
333 received significant criticism [1] mostly regarding an incomplete correction procedure of the dissolved
334 part of slag and the undissolved aluminosilicate hydrates. In this study the results were corrected for the
335 part of slag dissolved, although as pointed out in [1] this correction may only be valid for early hydration
336 ages. This is because the EDTA-soluble part of slag is expected to be the most reactive in paste. The
337 undissolved aluminosilicate hydrates were not taken into account, which most likely resulted in
338 underestimation of the results.

339

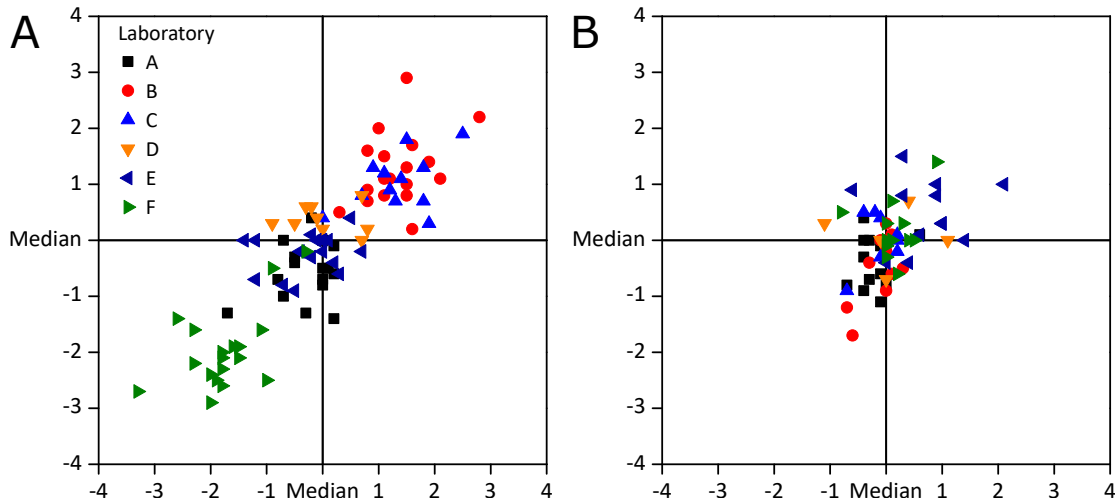
340 The selective dissolution technique based on salicylic acid + HCl could not be applied to the calcareous
341 fly ash due to its significant solubility in the acid mixture (20-30 wt.%). Nevertheless, the results obtained
342 for the siliceous fly ash (0.5-2.0 wt.% soluble) seem to agree quite well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

345 5.3 Consumption of portlandite analysed by mass-balance

346 One of the main sources of scatter in the results of this technique is the scatter in portlandite content
347 measured. As reported before in [1], because the reaction of slags and calcareous fly ashes consumes
348 little portlandite, a measurement error of ± 2 g portlandite /100 g anhydrous binder can lead to a relative
349 change in the degree of SCM reaction of around 50 %. Thanks to data available from several laboratories,
350 we assess the uncertainty of determination of portlandite consumption to separate the inter-laboratory
351 variation from the inherent precision of the thermogravimetric technique. Figure 4 shows a statistical
352 analysis of the results of portlandite content measured by the different laboratories using a modified
353 Youden plot. A full description of construction and interpretation of Youden plots is given in [16]. To
354 prepare Figure 4A:

- 355 • Compute the median of the absolute portlandite content for each mix and age.
- 356 • Compute the difference between each single measurement and its corresponding median.
- 357 • Assign randomly the computed differences as X or Y coordinate and plot the points. The number
358 of points in the plot is half the number of measurements.

359



360

361 Figure 4. Modified Youden plots showing scatter of the thermogravimetric results [g/100 g of anhydrous
362 binder] around their median values: (A) absolute portlandite content, (B) difference in portlandite
363 between PC-SCM and PC-Q reference.

364

365 Such construction clearly shows that in the absolute portlandite content measured the most important
366 difference results from an inter-laboratory bias and more specifically the way the tangential method is
367 applied to quantify the mass loss due to portlandite dehydroxylation. However, the bias in data treatment
368 is cancelled when differences of portlandite content are plotted instead of absolute values in Figure 4B.
369 The scatter in this figure is about ± 1.5 g/100 g of anhydrous binder, which demonstrates the accuracy of
370 the TGA and was roughly similar for all the participant laboratories. This scatter corresponds to
371 a maximum relative error in degree of reaction of roughly 40 %; in absolute terms, ± 10 % for a degree
372 of reaction of slag estimated at 25 %, for example.

373

374 A serious drawback of the calculation of SCM reaction by mass balance of portlandite consumption is
375 that it neglects the calcium provided to the pozzolanic reaction from the C-S-H formed from clinker
376 reaction. Decreasing Ca/Si ratios of the C-S-H measured in the presence of SCMs in Table 3 and in
377 literature e.g. [9,17] show that the reaction of the SCMs not only forms new C-S-H with lower Ca/Si
378 ratio, but also takes Ca from the existing C-S-H. This means that the consumption of portlandite observed
379 corresponds to much more SCM reaction than it would if no calcium was provided from the C-S-H.
380 Thus, it should not be surprising that the results obtained by analysis of portlandite consumption in Figure
381 2 are somewhat underestimated regardless of the SCM tested.

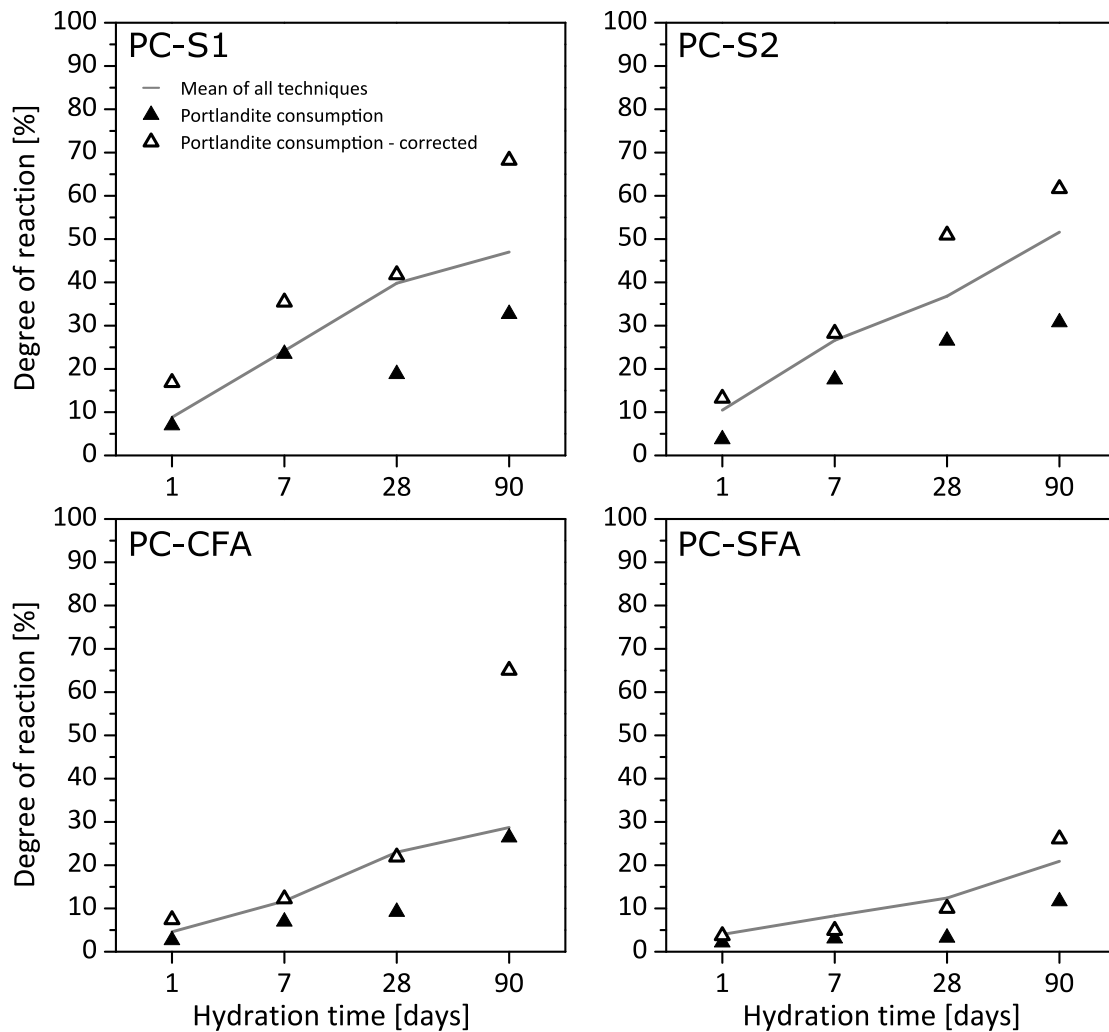
382

383 To account for the calcium provided from existing C-S-H it is necessary to measure the masses of C_3S
384 and C_2S reacted in the blended cement. One of the participant laboratories of this study carried out this
385 measurement using X-ray powder diffraction with Rietveld refinement. These masses were converted to
386 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
387 was assumed to be 1.85, the same as in the fly ash systems at 1 day hydration and similar to what can be
388 observed in plain Portland cement pastes [18]. The amount of calcium provided to the SCM reaction was
389 then calculated as a difference between this Ca/Si ratio and that measured in Table 3. The degrees of
390 reaction of the SCMs obtained in the aforementioned laboratory before and after correction are shown in
391 Figure 5. Although the mean does not take into account the updated values, it can be clearly seen that the
392 correction delivers more realistic values. In PC-CFA the value at 90 days seems much overestimated
393 though. Indeed, overestimation, especially at later ages, may be due to Ca being incorporated in AFm
394 and AFt phases, which is not taken into account here.

395

396 Accounting for the Ca provided from existing C-S-H makes the calculated values sensitive to the
397 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
398 degree of reaction of around $\pm 5\%$ to $\pm 10\%$ absolute.

399



400

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

404

405 From the above data, it is clear that this seemingly easy technique actually requires much more effort
 406 than a mere measurement of the portlandite consumption. Electron microscopy has to be carried out to
 407 measure the evolution of the Ca/Si ratio of the C-S-H and XRD-Rietveld analysis is required to estimate
 408 the amount of C-S-H formed from the reaction of clinker. The portlandite content can be measured by
 409 XRD-Rietveld instead of thermo-gravimetry.

410

411 5.4 SEM-image analysis

412 SEM-IA based on the segmentation of BSE grey levels was able to quantify the reaction of slags and that
 413 based on the segmentation of EDS full element maps according to [5] could measure the reaction of both
 414 the slags and the fly ashes. An SEM-IA of EDS full element maps has a further advantage of being able
 415 to resolve the reaction of different types of glass present in fly ash, which is impossible using the other
 416 methods.

417

418 Compared to the results of the other techniques in Figure 2 the SEM-IA tends to overestimate the degrees
419 of hydration of S2 and those of S1 at early ages and CFA at 90 days. This is due to general drawbacks
420 of microscopy: problems resolving fine particles and because random cross-sections of 3-dimensional
421 features are equal or smaller than their actual equatorial cross-sections. Further, SEM analysis is much
422 less available and it requires significantly more time and resources than the other techniques. Collection
423 of a representative array of BSE images for a single sample and hydration time can take up to around
424 2 hours. Eight EDS high quality full element maps take around 4 hours to measure with a modern fast
425 detector, while this type of data collection is far more time-consuming with older or benchtop
426 instruments. Preparation of flat-polished sections can take several days and good polishing is essential
427 to successful SEM analysis.

428 5.5 XRD-PONKCS

429 Among the techniques studied, by far the largest variations were observed for the XRD-PONKCS. For
430 PC-SFA the results of the different laboratories were much more comparable, most likely due to less
431 overlap between the "humps" of SFA and C-S-H, but also because the degrees of reaction were lower.
432 Some of the PONKCS results should have been discarded as nonsense outliers. It is clear that at the
433 present state of development this technique cannot give reproducible results between laboratories due to
434 different refinement techniques.

435

436 Contrary to the other techniques studied, there is no strict protocol of how PONKCS model phases should
437 be prepared and refined. The correct definition of the background is difficult, but limiting the number of
438 refined background parameters could improve the consistency of the results. Nevertheless, the major
439 problem seems to be the overlap of the SCM contribution with that of the C-S-H, which is particularly
440 important for slags. Indeed, in Figure 2 the variation of the PONKCS results was higher for slag mixes
441 and increased with hydration time, which seems to match with higher expected error due to more C-S-H
442 and less slag at higher hydration degrees. Published literature showed promising results of the PONKCS
443 method applied to synthetic mixes of SCMs and C-S-H [4], but it now seems that tackling real systems
444 is much more problematic. This problem may be even more important for low SCM replacement levels.
445 In the synthetic systems, for slag amounts below 10 wt.% at any hydration time the expected error was
446 2-3 wt.% and for the amounts below 5 wt.% the quantification was no longer valid. For an initial slag
447 content of 30 wt.% and 65% reaction after 90 days the remaining slag content would be around 10 wt.%
448 and the expected 3 wt.% error would translate to a variation in the degree of reaction of 10%. In real
449 systems, these values are expected to be much larger.

450

451 A decreased degree of reaction in PC-CFA after 90 days observed in Figure 2 may be due to another
452 issue. The model of an amorphous SCM phase used for PONKCS analysis is prepared on an anhydrous
453 SCM. However, fly ashes and in particular the calcareous ones may be composed of a variety of glasses
454 reacting at different rates [5]. This difference in reaction would affect the shape of the amorphous
455 background in XRD over the course of the reaction and lead to errors.

456

457 **6 Conclusions**

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

461

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

467

468 Selective dissolution of slag cement pastes based on EDTA + TEA + DEA slightly underestimated the
469 results compared to the other techniques, which is likely due to incomplete correction procedures. The
470 analysis of siliceous fly ash cement pastes using salicylic acid + HCl seems to work fairly well, while it
471 failed completely for the calcareous fly ash due to its high solubility in the acid mixture.

472

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

481

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

487

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

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502 **Compliance with Ethical Standards**

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506 **Conflict of Interest**

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

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553

554

555 Appendix1 – Experimental setups

556 Table 5. Experimental setup for the thermogravimetric experiments. In automated TGA experiments on
557 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

558

559 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

560

561 Table 7. Experimental setup for powder XRD measurements.

Instrument	Sample loading	Standard	Source	Angles/step $^{\circ}2\theta$ (CuK α)	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 α ₁ 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

562

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
<i>Calibrated on</i>	<i>anhydrous PC-S2 mix</i>	<i>anhydrous slag</i>	<i>anhydrous slag</i>	
Fly ash	n. a.	HKL file (P-1)	HKL file (1ma2)	A pseudo-Voigt peak
<i>Calibrated on</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 [19]	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>

564