

# TC 238-SCM: hydration and microstructure of concrete with SCMs

## State of the art on methods to determine degree of reaction of SCMs

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**Abstract** This paper is the work of working group 2 of the RILEM TC 238-SCM. Its purpose is to review methods to estimate the degree of reaction of supplementary cementitious materials in blended (or composite) cement pastes. We do not consider explicitly the wider issues of the influence of SCMs on hydration kinetics, nor the measurement of degree of reaction in alkali activated materials. The paper categorises the techniques into direct methods and indirect methods. Direct methods attempt to measure directly the amount of SCM remaining at a certain time, such as selective dissolution, microscopy combined with image analysis, and NMR. Indirect methods infer the amount of SCM reacted by back calculation from some other measured quantity, such as calcium hydroxide consumption. The paper first discusses the different techniques, how they operate and the advantages and limitations along with more details of case studies on different SCMs. In the second part we summarise the most suitable approaches for each

SCM, and the paper finishes with conclusions and perspectives for future work.

**Keywords** SCM · Hydration · Blended cement · Degree of reaction

### 1 Introduction and overview

A key question for the performance of blended (or composite) cements, containing a mixture of ground cement clinker, calcium sulfate (e.g. gypsum) and supplementary cementitious material (SCM) such as fly ash or blast furnace slag, is the extent of the reaction of the SCM in the mixture. This is complicated for several reasons:

1. The physical presence of SCMs is known to affect the rate and extent of the reaction of the ground clinker component—the so called “filler effect”, explained in more detail below.

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2. SCMs are usually amorphous with complex and varied mineralogies which make them difficult to quantify by many classical techniques such as X-ray diffraction.
3. The rate of reaction of an SCM in a cement blend may be quite different from the rate of reaction of the same SCM in systems containing simply alkali or lime.

In this paper, different methods that have been used to assess the degree of reaction of various SCMs are reviewed. The methods can be broadly categorized into *direct* methods, which aim to quantify the amount of unreacted SCM remaining and thereby the amount reacted, and *indirect* methods, which quantify other phases in the microstructure (e.g. portlandite, bound water) and thereby enable back-calculation of the degree of reaction of the SCM based on hypotheses about the reaction products of the SCMs. The accuracy of indirect methods depends on the accuracy of the hypotheses about hydration, but they will also usually contain a systematic error if they fail to take into account the filler effect.

It should be emphasized that all the studies described here relate to studies on pastes. In mortars and concretes the paste is diluted 3–4 times by the aggregates, with at least a corresponding increase in the errors on the estimate of the degree of reaction. Due to the difficulties and lack of precision of both direct and indirect methods, it has to be recognised that in practice the performance of most blends is still assessed by strength tests, which will not be considered in this paper.

The two SCMs most widely studied are blast furnace slag (or GGBFS (ground granulated blast furnace slag), referred to simply as “slag” in the following) and fly ash (from burning of coal to produce electricity). Most of the examples in this paper pertain to these materials. Silica fume has also been extensively studied. Work on other SCMs is sparse. In the absence of systematic studies, some general principles are discussed in the second part of the paper.

### 1.1 Filler effect

Before going further, it is important to clarify what is the so-called filler effect, which was studied by, for example, Gutteridge and Dalziel [35]; Cyr et al. [18]; Berodier and Scrivener [9, 10] where the simple physical presence of an SCM (or even an inert

material) will impact the reaction of the clinker phases. This effect has two components:

- (a) First, the substitution of clinker by an SCM at the same water to binder ratio implies a *dilution effect*. As there are fewer clinker grains, there is relatively more space for formation of the clinker hydrates and therefore the degree of reaction of the clinker component will be significantly higher than in the unsubstituted material. For example, Berodier [10] found that for pastes at an equivalent w/c ratio of 0.4, the degree of hydration in the plain Portland cement pastes was around 80 % at 28 days, compared to 90 % in blends containing 30 % quartz or fly ash.
- (b) The second effect is that the surfaces of the SCM may act as *nucleation sites* for hydrates. Berodier [9] showed that this effect is relatively minor for SCMs with a similar particle size distribution to that of Portland cement, but it can be important for fine materials such as silica fume, which has a significant acceleration effect on the hydration of the clinker (e.g. [35, 36], Rossen [62]).

## 2 Direct methods

As already mentioned, SCMs (with a few exceptions, such as zeolites [70]) contain usually high amounts of amorphous phases and so cannot be quantified easily by X-ray diffraction. Nevertheless, conventional X-ray diffraction is an important method to quantify the crystalline phases present as will be discussed in the section on mass/volume balance under indirect methods. Furthermore, new techniques to estimate poorly crystalline phases by X-ray diffraction hold promise as direct methods as described later. In addition, three other methods to measure directly the degree of reaction of SCMs will be discussed in this section:

1. Selective dissolution
2. BSE image analysis
3. NMR

### 2.1 Selective dissolution

This is the oldest and most widely used method developed to measure the reaction of SCMs. The



intention of such methods is that the unreacted clinker phases and the hydrates from the clinker and SCMs are dissolved, leaving only the unreacted SCM as a residue. Methods have mainly been developed for fly ash and slag. Opinions are divided about their accuracy as can be seen in the following discussion. Recent studies of residues by X-ray diffraction and SEM reveal that significant amounts of clinker and hydrate phases may remain after dissolution [7, 33, 51]. It has been claimed in the literature that correction for the effects of incomplete dissolution is possible. However, recent work [7, 33, 44] indicates that large, non-quantifiable, systematic errors will remain, as the adoption of different assumptions can lead to large differences in the quantity of fly ash or slag reacted. It is very

difficult to ensure a protocol that can be reproduced in different laboratories; while it is comparatively easy to define the amounts of solution, lengths of time, and other specified parameters the most difficult factor to control will be the grinding of the samples and thus the particle size distribution of the reacting paste. This means that while good results (at least on a comparative basis) may be obtained within one laboratory, it is not really possible to compare results obtained by different laboratories.

Table 1 summarises the most important selective dissolution methods applied to slag and fly ash, with the principal references. Some of the most widely used methods are discussed below in more detail.

**Table 1** Description of the different selective dissolution methods

Methods	Chemicals needed/1 g sample	Stirring time (min)	References	SCM
EDTA NaOH	500 ml disodium EDTA·2H <sub>2</sub> O (0.05 M) in NaOH (0.1 M)	60	Luke and Glasser [51]	Slag
	500 ml distilled water		Dyson et al. [24]	Slag
	50 ml (1:1) triethanolamine: water		Ben Haha et al. [7]	Fly ash
	125 ml NaOH (1 M) to adjust pH		Kocaba et al. [44]	Slag
EDTA DEA	25 ml triethanolamine	120	Lumley et al. [52]	Slag
	50 ml water		Ben Haha et al. [7]	Fly ash
	9.3 g disodium EDTA·2H <sub>2</sub> O			
	17.3 ml diethylamine			
	Fill to 100 ml with distilled water			
	Before extraction, dilute 100 ml of the solution to ~1,600 ml with distilled water			
Salicylic acid	6 g salicylic acid	180	Ohsawa et al. [56]	Fly ash
	40 ml methanol		Luke and Glasser [51]	Slag
			Ben Haha et al. [7]	Fly ash
Hydrochloric and salicylic acid	5 g salicylic acid	30	Suprenant and Papadopoulos [73]	Fly ash
	4.2 ml hydrochloric acid		DIN [21]	Fly ash
	Diluted to 100 ml with methanol		Ben Haha et al. [7]	Fly ash
Hydrochloric acid	250 ml (1:20) hydrochloric acid	180	Fernández-Jiménez et al. [27]	Fly ash
Picric acid	11 g picric acid	40	Ohsawa et al. [56]	Fly ash
	60 ml methanol		Li et al. [49]	Fly ash/ silica fume
	40 ml distilled water		Baert [6]	Fly ash
			Ben Haha et al. [7]	Fly ash

**Table 2** Insoluble residue of GGBS samples from different European countries (partly published in Vollpracht et al. [77])

No.	Producing country	EDTA residue (% by weight)	(CaO + MgO)/SiO <sub>2</sub> (mass ratio)
1	Germany	79.5	1.54
2	Germany	82.9	1.44
3	Germany	86.8	1.44
4	Germany	89.5	1.39
5	Germany	92.5	1.34
6	Germany	86.6	1.42
7	Germany	94.6	1.30
8	Germany	87.9	1.33
9	Germany	85.4	1.33
10	Austria	92.6	1.19
11	Austria	92.1	1.20
12	Austria	83.8	1.06
13	Austria	78.1	1.07
14	Austria	92.1	1.20
15	Poland	70.7	1.26
16	Ukraine	58.9	1.39
17	Czech Republic	52.3	1.32

### 2.1.1 EDTA method for slag

The most widely reported selective dissolution method is the selective dissolution in EDTA solution to determine the unreacted slag remaining in a blended paste. Several variants of this method have been proposed where NaOH, TEA or DEA are also added to the EDTA solution. Details of the procedures can be found in the references given in Table 1. For the determination of the quantity of slag in an anhydrous blended cement the procedure has also been standardized in Germany [21].

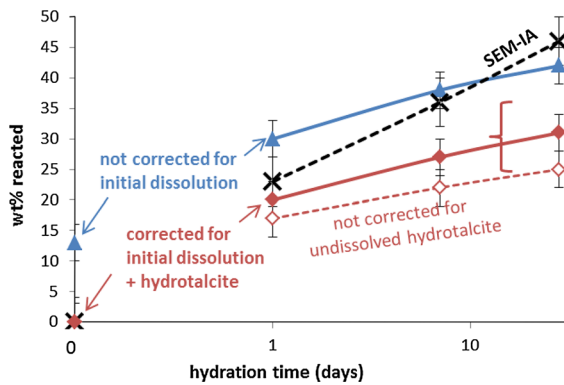
As already indicated, the main question is the selectiveness of the dissolution; clinker phases and hydrates should be dissolved, and the unreacted slag not. It is acknowledged that this selectivity is not 100 %, and various procedures have been put forward to correct for the errors. For example, in the DIN technical report [21] the values for anhydrous cements are multiplied by 1.05 to account for the fact that some of the slag dissolves. However, as shown in Table 2, the actual amount of slag that dissolved varies significantly, from <5 % to >45 %, depending on the source of the slag. The digestion was performed as described in Table 1 (line EDTA DEA). If the pure slag is available then the values can be corrected more accurately by conducting parallel dissolution tests on the unreacted material, but this is not always possible.

For hydrated materials, other corrections must be applied to account for the fact that not all the hydrates dissolve, but a residue remains of hydrotalcite like phase and alumino-silicate hydrates [7, 24, 30, 33, 48, 51, 52]. Thus, for example, Lumley et al. [52] suggested to correct the undissolved fraction for the formation of hydrotalcite like phase. The mass of hydrotalcite like phase formed from the reacted slag was calculated as  $2.35 \times M$ , with  $2.35^1$  (=molar mass hydrotalcite/molar mass MgO =  $473.7/40.3 = 2.35$ ) and  $M = \text{MgO}$  content of the slag.

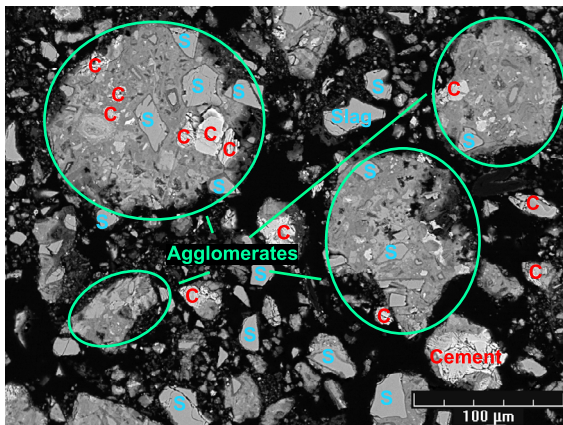
Applying both of these correction factors, Fig. 1 shows the corrected and uncorrected results for a super-sulfated slag subjected to selective extraction by EDTA (data from Gruskovnjak et al. [33]) compared with results from BSE image analysis (see later). This suggests that the correction for the part of the slag dissolved is valid at early ages, but not at later ages. This can be explained as the fraction of the slag dissolved during the selective extraction probably corresponds to the most reactive fraction, which will most probably react first in a blended system.

<sup>1</sup> This value assumes the formula  $\text{Mg}_5\text{Al}_2(\text{OH})_{14}(\text{CO}_3)$  and should be adjusted accordingly if the hydrotalcite composition is believed to be different.





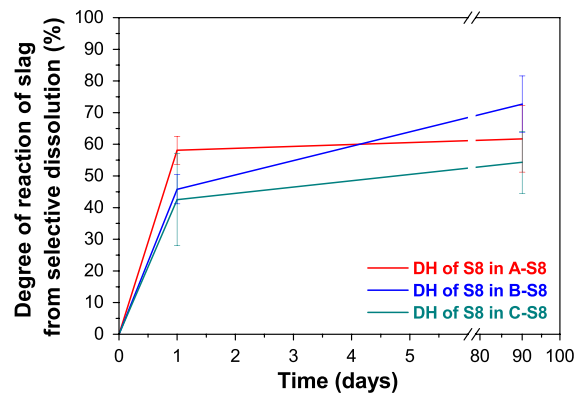
**Fig. 1** Influence of the correction for (i) the presence of undissolved hydrotoalcite and (ii) the amount of unhydrated slag dissolving during EDTA extraction on the calculated degree of slag reaction, and comparison with the degree of reaction obtained by SEM image analysis (SEM-IA), for a super-sulfated slag. For this slag 13 % dissolved when tested before hydration, which is in a similar range to many slags used worldwide. The error bars show variations for repeat measurements. Data from Gruskovnjak et al. [33]



**Fig. 2** BSE image of a cement–slag blend hydrated 90 days, after selective dissolution (C cement and S slag). From Kocaba et al. [44]

However, the correction procedure shown in Fig. 1 is still incomplete, as it neglects the undissolved aluminosilicate hydrates which remain present after the extraction. Thus, even after correction for the hydrotoalcite like phase the degree of slag reaction is probably underestimated.

These two effects, dissolution of part of the unreacted slag and failure to dissolve some hydrate phases, are the main sources of error identified. A BSE image from Kocaba et al. [44] shows undissolved clinker phases and hydrates in the residue from selective dissolution (Fig. 2). Attempts were made to



**Fig. 3** Degree of reaction of slag by selective dissolution technique measured by Kocaba et al., for details see Kocaba et al. [44]

correct for these effects, but unrealistically large degrees of reaction (40–60 % at one day) were obtained (Fig. 3).

As a result, considerable uncertainty is associated with application of selective extraction procedures to hydrated cements, which may contain other factors in addition to the two main ones discussed earlier. The typical error in the calculation of the degree of reaction will be at best of the order of  $\pm 10$  % (absolute).

### 2.1.2 Salicylic acid methods for fly ash

In the early 1980s the CEN/TC 51 accepted a selective dissolution method to determine the fly ash content of mixed cements. In 1987 the method was standardised (DIN EN 196-4:1987-01). The standard was withdrawn 3 years later and replaced by a draft standard. This draft was never implemented. Today the same method is described in a technical report from the German Institute for Standardisation DIN [21].

The method differs in several respects from the salicylic acid–methanol treatment described by Ohsawa et al. [56]. Ohsawa et al. did not add hydrochloric acid, and the concentration of salicylic acid was three times higher.

The CEN method has been widely used to determine the fly ash content of Portland fly ash cements, e.g. in the context of the technical approvals for this kind of cements in Germany in the 1980s. Apart from the pozzolan there are some other components of the Portland cement (mainly sulfate) that are insoluble in the acid mixture. Therefore the residue should be analysed for its sulfate content ( $\text{SO}_3$ ) and corrected accordingly.

The method has also been used to determine the degree of reaction of hardened cement pastes (e.g. [78]). Tests on hardened cement paste without fly ash demonstrated that C–S–H, remaining clinker and blast furnace slag are almost completely dissolved. The sulfate bearing phases like ettringite or monosulfate are also dissolved, but then reprecipitate as gypsum. During the drying of the residue, bassanite is formed; therefore the sulfate correction that is made on cements is also necessary for hydrated samples. For example, the following results were obtained for pastes without fly ash (additional information to Vollpracht [78]):

CEM I: residue:  $4.6 \pm 0.2$  wt% after correction for bassanite:  $0.9 \pm 0.4$  wt%

CEM III/A: residue:  $4.6 \pm 0.3$  wt% after correction for bassanite:  $1.3 \pm 0.3$  wt%

The CEN method was applied to hardened cement paste with different amounts of fly ash [78], from 1 day up to more than 10 years. At long ages (approx. 12 years) the degree of reaction of the fly ash depended on the content of fly ash in the binder as shown in Table 3.

These results are plausible, but the degrees of reaction were not verified by other direct methods. Therefore the possibility cannot be ruled out that some of the fly ash was dissolved as well, so the degree of reaction might be somewhat overestimated.

### 2.1.3 Picric acid methods for fly ash

In addition to the salicylic acid method discussed above, another method that can potentially work well with fly ashes is based on picric acid. However, it is important to note that some compounds and reaction products of **picric acid can pose a severe explosion hazard**, in particular the dried residues which form around the caps of improperly-stored bottles of this liquid over time, as well as many picrate salts. This

intrinsic hazard means that it is difficult to recommend the use of picric acid as a routine analytical method.

The accuracy of this method has been investigated by Ohsawa et al. [56]. They evaluated various kinds of selective dissolution: using either successive treatments of HCl and Na<sub>2</sub>CO<sub>3</sub>, picric acid–methanol solution with or without water, salicylic acid–methanol solution with or without water, or salicylic acid–acetone–methanol solution. Using HCl and Na<sub>2</sub>CO<sub>3</sub> solutions sequentially, nearly 20 % of fly ash was found to dissolve, while salicylic acid-containing solutions did not sufficiently dissolve the hydration products. The technique with picric acid–methanol and water was considered the best compromise between dissolving the hydration product enough, but not too much of the fly ash. It gave reproducible results (coefficient of variation of 0.23–0.55 % for the degree of reaction on duplicate measurements) and was less time consuming. Grinding the fly ash before adding it to the picric acid–methanol solution did not markedly change the results from those on non-ground fly ash. Later researchers attempted to reproduce and modify the experiments of Ohsawa et al. [25]; [49, 73] focusing on the picric acid–methanol and water solution as well as on salicylic acid combined with hydrochloric acid and methanol, to dissolve the cement portion of a blend. They concluded that selective dissolution is viable when more than 90 % of the cement dissolves, less than 10 % of the fly ash goes into solution [73], and correction factors for these effects are applied.

Table 4 shows the dissolved percentage of different types of cement and fly ash, used by Baert [6], after subjecting each of them separately to the selective dissolution method in picric acid–methanol–water.

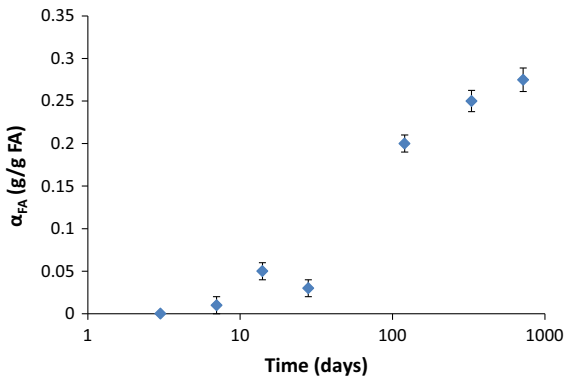
**Table 3** Reaction degree of fly ash in pastes with Portland cement after approx. 12 years of hydration [78]

Proportion of FA in the binder (% by weight)	Reaction degree of the FA (%)
20	42.4
40	32.4
60	26.1

**Table 4** Dissolved percentage of cement and fly ash when dissolved in picric acid with methanol solution and water from Baert [6]

Material	Dissolved percentage (%)
C(I)	93
C(II)	92
C(III)	96
Fly ash (1)	13
Fly ash (2)	11
Fly ash (3)	6
Fly ash (4)	8





**Fig. 4** Reaction degree of fly ash in paste with 50 % C(I), 50 % fly ash (1) and a water-to-binder ratio of 0.40. From Baert [6]

From Table 4 it can be seen that the latter solution indeed dissolves more than 90 % of the different Portland cement types C(I), C(II) and C(III). However, for some fly ashes [fly ash (1) and fly ash (3)] somewhat more than 10 % is dissolved.

Figure 4 shows the results obtained by Baert [6] for the reaction of fly ash using the picric acid method, where fly ash (1) (from Table 3) was used as 50 % replacement material of cement C(I) in a paste with water-binder ratio of 0.40. The fly ash reaction seems to become significant from 14 days onwards. At 28 days the measured reaction degree of fly ash is lower than that determined at 14 days, which indicates accuracy problems related to the selective dissolution. Around 2 years, the measured reaction degree  $\alpha_{\text{fly ash}}$  was 28 %.

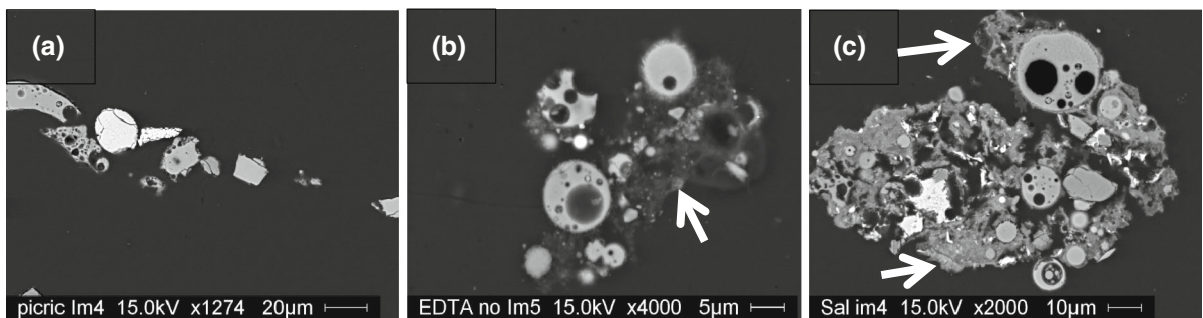
For fly ash used in the study of Ben Haha et al. [7] it was observed that while the picric acid method (Table 1) dissolved nearly all (98 %) of the Portland

cement, it also dissolved 18 % of the unhydrated fly ash, which will lead to a large uncertainty in the calculated degree of fly ash reaction, similar to the case discussed above for slag, during the EDTA extraction procedure. This was confirmed in a BSE study of the residues of a 90 day hydrated cement paste where no undissolved hydrates or clinker were observed, but also no small fly ash particles remained after the selective dissolution (Fig. 5).

#### 2.1.4 Comparison of selective extraction methods

Ideally an extraction method should completely dissolve the anhydrous Portland cement and the hydrates, while the unreacted SCM should not dissolve at all. These requirements are not fulfilled for any of the methods studied. Picric acid, and EDTA with NaOH or with DEA dissolved virtually all of the Portland cement, but also dissolved a considerable part (10–20 wt%) of the fly ash. In contrast, the salicylic acid method leaves a large fraction of the Portland cement undissolved. Both the dissolution of the unhydrated fly ash and the incomplete dissolution of the Portland cement clinker will lead to a large uncertainty in the reaction degree at longer hydration times as illustrated in Table 5.

Examination of the residue after extraction of the hydrated blend showed clearly the differences between the different extraction methods (Fig. 5). The residue of hydrated paste using picric acid consisted only of unreacted fly ash particles; no residues of hydration phases or unreacted clinker grains were found. However, up to 20 % of the unreacted fly ash was also dissolved which is expected to lead to large



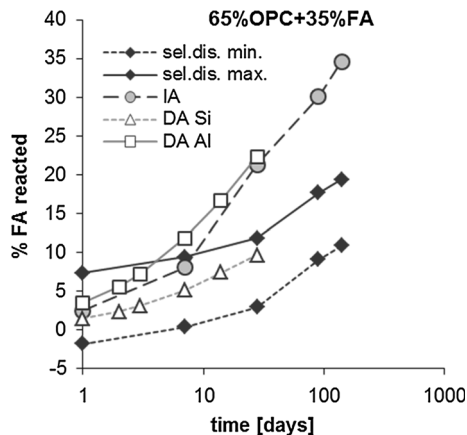
**Fig. 5** Backscattered electron (BSE) images of the residue of hydrated blended cement paste after selective dissolution with **a** picric acid, **b** EDTA-NaOH, **c** salicylic acid. From Ben Haha

et al. [7]. *Arrows* indicate residue of hydrates and undissolved clinker in the case of EDTA-NaOH and salicylic acid

**Table 5** Results of selective dissolution: mass of the residue as a % of the initial mass, and degree of fly ash reaction after 3 months

Method	Picric acid	EDTA NaOH	EDTA DEA	Salicylic acid	Salicylic acid + HCl
Time	40 min	1 h	2 h	3 h	30 min
Cement	1.7	2.2	1.9	36.6	10.0
Fly ash	82.5	92.2	90.7	96.9	93.4
80 PC 20 fly ash (3 months)	12.2	17.2	15.8	47.2	22.2
Fly ash reaction min	32	15	20	3	17
Fly ash reaction max	43	21	27	4	21

*Min* corrected for initial reaction of the fly ash, *max* uncorrected. From Ben Haha et al. [7]



**Fig. 6** Percentage of fly ash reacted determined in a blended cement containing 35 wt% fly ash using different methods: selective dissolution using EDTA/NaOH (denoted sel. dis., where the *max* and *min* curves use different assumptions around the nature of the residue), image analysis (IA), and fly ash dissolution in diluted solutions containing 0.5 mol/l NaOH (based on the measured Al or Si concentrations; DA Si or DA Al). From Ben Haha et al. [7]

uncertainties at later ages. In addition, due to the hazardous nature of the picric acid this method is not recommended.

For the two EDTA methods a residue rich in Mg, Al and Si was observed. The salicylic acid method failed to sufficiently dissolve the hydrates and the clinker minerals. The combination of salicylic acid with HCl improved the dissolution of the hydrates and the clinker, but a residue rich in calcium and sulfate (bassanite) was observed; this can be corrected for, as discussed in Sect. 2.1.2.

Ben Haha et al. [7] concluded that the picric acid method and the EDTA NaOH extraction would provide the best results, and preferred the EDTA NaOH extraction due to the hazardous nature of the picric acid. Figure 6 compares the reaction degree of

fly ash in blended cement determined by selective dissolution (using EDTA NaOH) and by image analysis (IA), with the reaction of the fly ash in 0.5 M NaOH solution (DA), which was designed to have the same pH as the pore solution. At early ages it seems appropriate to correct the selective dissolution results for the amount of fly ash dissolved during the test. At later ages the reactive and/or very small particles originally present in the fly ash will have reacted completely, such that this correction is no longer needed. This conclusion is similar to the case of supersulfated slag as discussed earlier and shown in Fig. 1. The percentage of reacted fly ash determined by selective dissolution, where a significant amount of hydrates remained in the residue, was generally lower than the values obtained by image analysis (although image analysis for fly ash is less accurate than for slag due to the heterogeneity and the small particle size of the fly ash, as will be discussed in Sect. 2.2). The results of image analysis agree well with the dissolution kinetics of fly ash observed in alkaline solutions with the same pH as the pore solution of the paste.

The treatment of SCMs with acidic solutions will lead to leaching of soluble elements such as alkalis and Ca from the SCM glass, leaving a leached layer or residue enriched in less soluble elements such as Si and Al. Leaching may thus affect the mean structure of the residue (as indicated by the NMR results of Dyson et al. [24]) and would bias the determination of the degree of reaction. However, dissolution in alkaline solutions, as in the real case of reaction in blended cements, does not generally result in significant leached layers [37].

## 2.2 BSE image analysis

Backscattered electron images of polished sections, obtained in an SEM, allow many features of the



microstructure to be identified and quantified according to their brightness [65], which depends on their average atomic number. Several studies have shown that the amount of unreacted cement measured in this way corresponds well to the other independent measures of degree of hydration, for example X-ray diffraction with Rietveld analysis [64, 66].

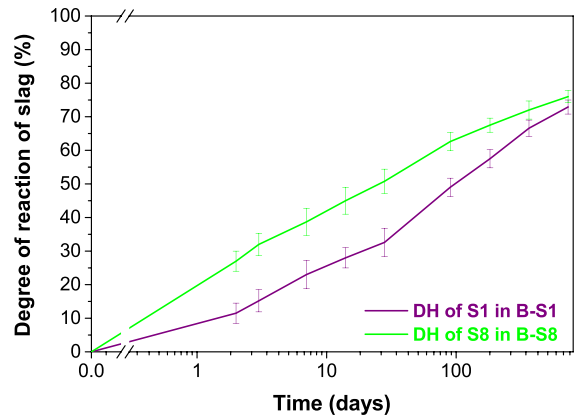
### 2.2.1 Slag

The amorphous component of a slag generally has a homogeneous grey level, which should allow it to be identified by image analysis. Brough and Atkinson [11, 12] demonstrated the potential of this method to measure the degree of reaction of slag in materials activated by alkalis. Kocaba et al. [44] made a detailed study of this method to measure the degree of reaction of slag in blended cements of slag and Portland cement. The main difficulty encountered was that the grey levels of common slags are very similar to that of calcium hydroxide. For some slags it is possible to distinguish the two phases through application of image processing filters, but more generally it is better to combine BSE images with chemical mapping by EDS, using the fact that slag contains aluminium and magnesium while portlandite does not. In the past, this method was not practical, as with classical silicon drift detectors a map with reasonable resolution would take at least 1 h to acquire. With the availability of new fast detectors, reasonable maps can be acquired in around 5–10 min and it is possible to collect 50–100 images automatically overnight.

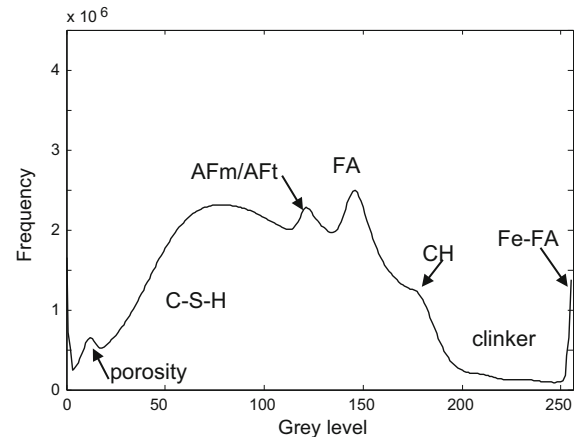
Figure 7 shows the results obtained by Kocaba et al. [44] for two slags of quite different composition, each in a blend of 60 % Portland cement with 40 % slag. The error bars were obtained by making several independent determinations on the same sample. These results show a progressive reaction of the slag, as expected, and correlate very well with the progress of reaction obtained from the calorimetry method described later.

### 2.2.2 Fly ash

Due to the heterogeneous composition of fly ash, it contains phases with many and varied grey levels, which overlap with hydrates or clinker phases. Nevertheless, in the samples studied by Ben Haha et al. [7] and Deschner et al. [20] it was possible to identify a



**Fig. 7** Degree of reaction of slag in 40 % slag blend from SEM-BSE-IA-mapping. From Kocaba et al. [44]



**Fig. 8** Representative histogram of BSE images of Portland-fly ash blend after 28 days of hydration. From Deschner et al. [20]

peak in the histogram of the samples that could be attributed to the major part of unreacted fly ash (FA in Fig. 8). This was used as a basis for the grey level segmentation. Additionally, the histogram (Fig. 8) shows peaks correlating to porosity, hydrate phases, clinker and high iron content components of the fly ash.

Due to the high heterogeneity of the grey level and the shape of fly ash particles, an elaborate procedure using a combination of grey level thresholding and different morphological filters was applied to distinguish between the unreacted fly ash and the hydrated phases, as described in more detail in Ben Haha et al. [7] and Deschner et al. [20].

The standard deviation of the determination of the reaction degree of the fly ash based on separate sets of measurements on different samples was around 5 %,

despite the fact that a relatively small area is investigated and the heterogeneity of the sample would be expected to be one of the main sources of error. There is also a systematic error due to the presence of very small fly ash particles ( $<1 \mu\text{m}$ ), which are not detected by the image analysis procedure, as discussed further below. These methods were adapted to the specific fly ashes studied and cannot be generalised to all fly ashes given their variability. The study by Durdzinski et al. [23] described below, looks at how this variability can be characterised as illustrated in Fig. 9 which shows the different population of phases (amorphous and crystalline) in two fly ashes of nominally similar composition.

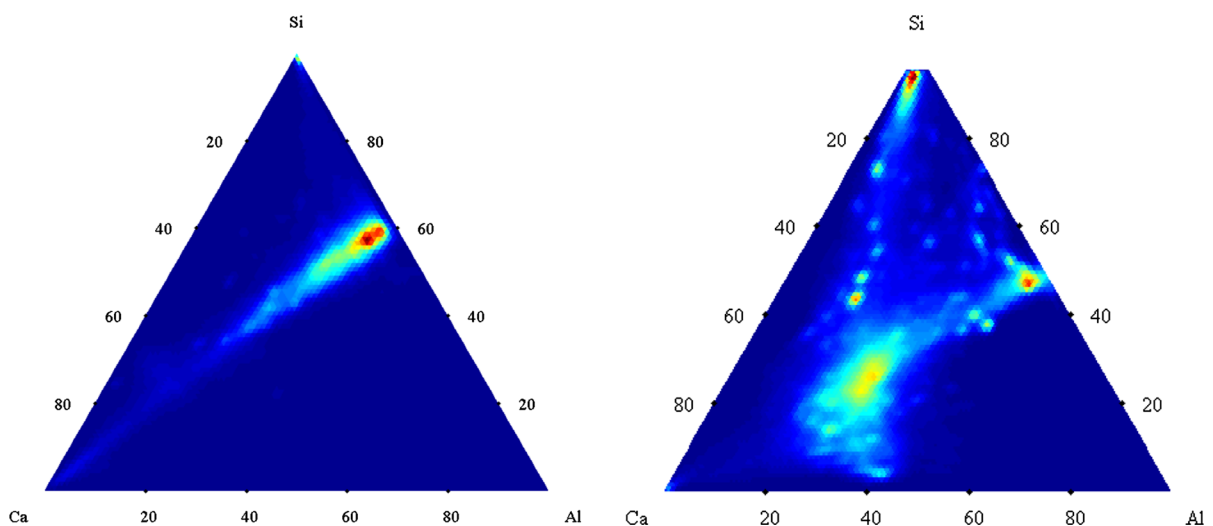
Recently Durdzinski et al. [23] proposed a new method to analyse SCMs (particularly fly ash) in blended materials based on full chemical mapping. Data can be visualised, for example, in ternary frequency plots such as for the main components  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$  as illustrated in Fig. 9. This enables different categories of glass to be identified, and each category can then be mapped back onto the BSE image or further analysed for minor elements (e.g.  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{MgO}$ , and others). This method can then be used to assess the degree of hydration for each of the different categories, as shown in Fig. 10. As noted above an error will arise due to the fact that small particles are not measured. However, it is estimated from the particle size distribution curve of the fly ash that the amount of material below the size threshold for detection is around 3 %. The relatively

smooth evolution of the degree of hydration indicates that, despite the heterogeneity of the fly ash and the relatively small number of images analysed, the errors in the estimates of the degree of hydration are only around 3–5 %.

These new results indicate that the information which can be obtained from fast EDS mapping has the potential to revolutionise the characterisation of fly ash and the measurement of the degree of hydration.

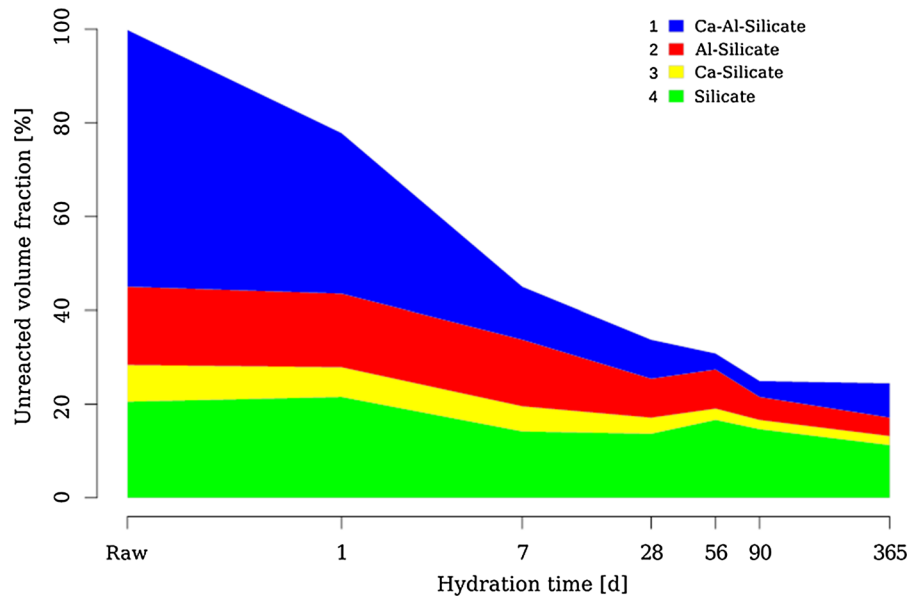
### 2.2.3 Statistics of image analysis

An important aspect of image analysis is the number of images analysed. The number needed to achieve a reasonably accurate measurement (say  $\pm 5\%$ ) will vary with the nature of the SCM, the replacement level, the magnification of the images and the heterogeneity of the sample. So for a paste with a fairly high replacement level (range 30–40 %), a homogeneous SCM and an image width of around  $300 \mu\text{m}$ , reasonable accuracy can be obtained with maybe only 10–20 images. At the other extreme, for a concrete with a lower replacement level (say 10 %) at a similar magnification, 100–200 images may be needed to obtain the same accuracy. In practice the best method to estimate the error is to make several sets of measurements on the same sample, or better still on several samples from the same mixture, and calculate the error from the variation in these measurements. It should be noted that there is a direct equivalence between the area fraction measured on sections and the



**Fig. 9** Al-Si-Ca frequency plots of the EDS data for two fly ashes From Durdzinski et al. [23]

**Fig. 10** Reaction of different glasses in a fly ash in a blended cement determined by fast EDS mapping. From Durdzinski et al. [23]



volume fraction (Delese principle) provided the materials is statistically isotropic.

### 2.3 NMR

Solid-state magic-angle-spinning (MAS) NMR spectroscopy has been used in several studies to follow the hydration of the principal clinker phases in Portland cement along with the degree of hydration for SCMs in Portland cement-SCM blends. In addition to degrees of reaction, valuable information on the structure of the C–S–H phase and how this is affected by SCMs in hydrated Portland cement-SCM blends can be derived from the NMR spectra, although this will not be discussed in detail here; for a brief introduction to MAS NMR studies of cementitious systems, see Skibsted et al. [68]. The method is nuclear-spin ( $I$ ) selective, since one nuclear spin isotope of the NMR periodic Table ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$ ,  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$  etc.) is detected at a time. The observed resonances for a given NMR isotope depend on the local electronic structure and mainly reflect the few nearest coordination spheres. Thereby, NMR complements other analytical techniques that probe long-range order of crystalline materials or bulk structural features. More importantly, the dependency on only the nearest chemical environments implies that crystalline and amorphous components are detected in an equal manner, which is one of the main strengths of solid-state NMR in studies of cementitious materials. The

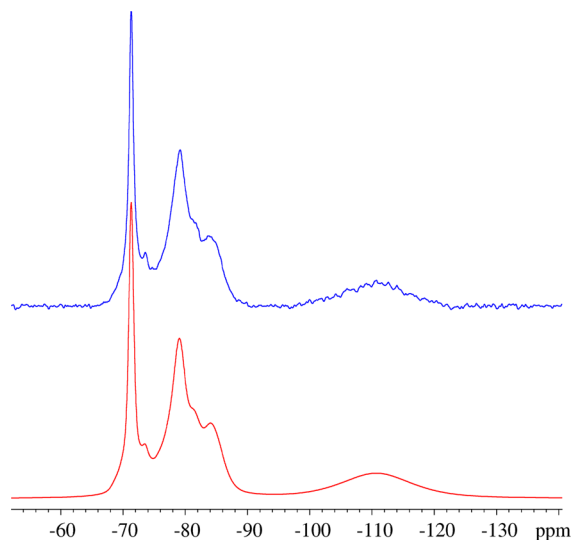
technique has been used to follow the reactivity of a range of SCMs in hydrated cement blends, including silica fume, slags, fly ashes, natural pozzolans, glasses, metakaolin and other calcined clays.

NMR studies of the degree of clinker and SCM reaction in cement blends have almost exclusively used either  $^{29}\text{Si}$  ( $I = 1/2$ , 4.7 % natural abundance) or  $^{27}\text{Al}$  ( $I = 5/2$ , 100 % natural abundance) as structural NMR-spin probes. The experiments employ typically 0.05–0.25 g of sample in a powdered form, where the hydration of the hydrating material has usually been stopped at appropriate time intervals prior to analysis by suspending the ground sample in isopropanol or acetone, to remove water, followed by gentle drying. The need for fast rotation of the sample (e.g. 3,000–15,000 rotations per second) during the MAS NMR experiment provides an unrealistic environment for in situ hydration studies. Moreover, and in particular for  $^{29}\text{Si}$  MAS NMR experiments, the sensitivity and resulting signal-to-noise-ratio, which principally depends on the nuclear spin properties ( $I$  value, natural abundance, and gyromagnetic ratio), the magnetic field strength and the number of repetitions, is so low that concrete samples can hardly be investigated, and thus the majority of studies have been done on paste samples. The  $^{29}\text{Si}$  chemical shift reflects principally the condensation of  $\text{SiO}_4$  tetrahedra ( $Q^n$ ,  $n = 0-4$ ), allowing observation of distinct resonances from alite, belite ( $Q^0$ ), the C–S–H phase ( $Q^1$ ,  $Q^2$ ) and additives such as clays ( $Q^3$ ) and silica

fume ( $Q^4$ ).  $^{27}\text{Al}$  MAS NMR provides mainly information about the aluminate coordination state, since distinct resonances are observed for Al in tetrahedral, five-fold and octahedral coordination. Most anhydrous cement minerals and SCMs include Al in tetrahedral coordination while hydrated calcium aluminate phases contain octahedrally coordinated Al. The low natural abundance of the  $^{29}\text{Si}$  isotope along with potentially long spin–lattice relaxation times makes  $^{29}\text{Si}$  NMR experiments time consuming, and overnight experiments are often required to achieve spectra with good signal-to-noise ratios. These factors are less critical in  $^{27}\text{Al}$  NMR where high-resolution spectra typically can be achieved within 1 h for a Portland cement with a bulk  $\text{Al}_2\text{O}_3$  content of 2–5 wt%.

A critical factor for all NMR experiments is the content of paramagnetic ions in the material (i.e.  $\text{Fe}^{3+}$  in cements), since the unpaired electron of these ions results in a strong electron–nuclear dipolar coupling with the observed nuclear spins. This coupling provides a very efficient relaxation mechanism, reducing the detected magnetisation in the experiment and thereby the quantitative reliability of the measurement. This effect has been evaluated in  $^{29}\text{Si}$  MAS NMR of anhydrous Portland cements [60] where it was found that quantitative results can be achieved for cements with a bulk  $\text{Fe}_2\text{O}_3$  content below approx. 5 wt%  $\text{Fe}_2\text{O}_3$ . Although the line broadening effect from the unpaired electron–nuclear spin couplings will be reduced by fast magic-angle spinning, this interaction may prevent quantitative studies of SCMs containing high contents of iron such as fly ashes.

The ability to quantify the degree of SCM reaction by  $^{29}\text{Si}$  NMR was pioneered in studies of Portland cement-silica fume blends [22, 38, 39]. The amorphous nature of silica fume results in a broad  $^{29}\text{Si}$  NMR resonance ranging from  $-100$  to  $-125$  ppm (Fig. 11) that does not overlap with the resonances from alite, belite or C–S–H. Thus, for a hydrated cement blend the fraction of  $^{29}\text{Si}$  spins in silica fume as a function of time [ $I_{\text{SCM}}(t)$ ] can be determined by spectral integration and the degree of reaction calculated,  $H = [1 - I_{\text{SCM}}(t)/I_{\text{SCM}}(0)]$ , by comparison with integral values for the anhydrous blend [ $I_{\text{SCM}}(0)$ ]. The early  $^{29}\text{Si}$  NMR studies of Portland cement-silica fume blends showed that high degrees of silica fume reaction ( $H > 65\%$ ) are observed after prolonged hydration (e.g. 3 months) at low replacement levels (10 wt%), and that silica fume accelerates the early



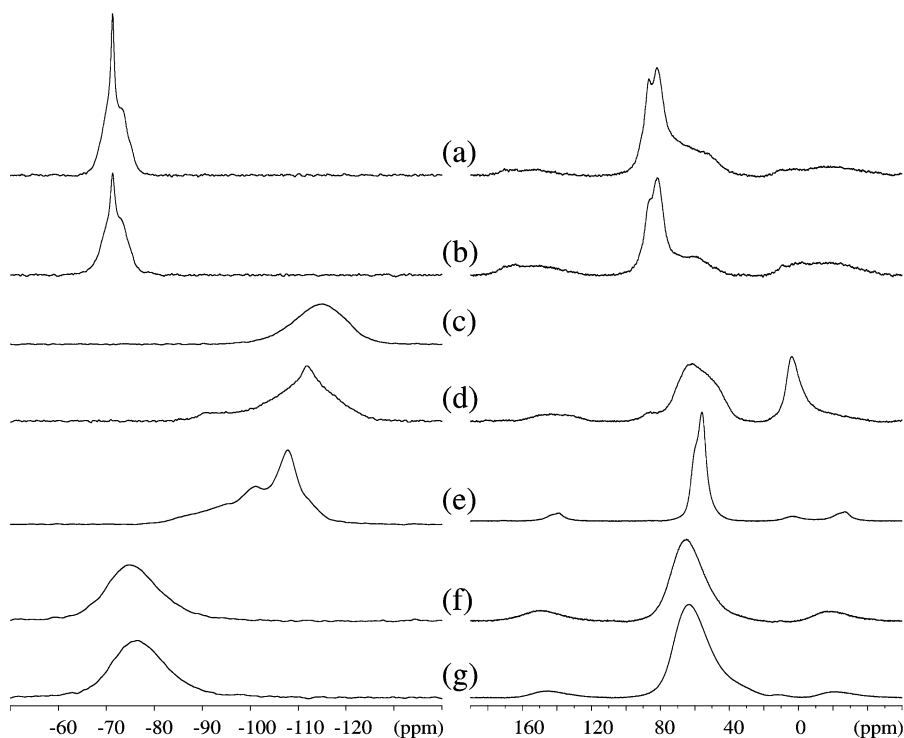
**Fig. 11**  $^{29}\text{Si}$  MAS NMR spectrum of a white Portland cement–silica fume blend (90:10 w/w) hydrated for 3 days. The optimum simulation is shown below the experimental spectrum, obtained using sub-spectra for alite, belite, silica fume and the  $Q^1$ ,  $Q^2(1A)$ , and  $Q^2$  resonances of the C–S–H phase. From Poulsen [59]

hydration of alite, the latter ascribed to the small silica fume particles acting as nucleation agents for the C–S–H phase (see discussion of the filler effect in Sect. 1.1).

$^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR spectra of silica fume, a fly ash with low iron content (0.4 wt%), a natural pozzolan, and two different slags are shown in Fig. 12 [59]. The  $^{29}\text{Si}$  MAS NMR spectra of the fly ash and natural pozzolan each cover spectral ranges of more than 35 ppm, reflecting the presence of several different  $Q^2$ – $Q^4$  silicate species in these SCMs. This may lead to partial overlap of the resonances from the SCMs (e.g. the natural pozzolan,  $-80$  to  $-115$  ppm) with the peaks from the C–S–H phase ( $-75$  to  $-88$  ppm) in hydrated Portland cement blends, as becomes apparent from a comparison of the  $^{29}\text{Si}$  MAS NMR spectra of the anhydrous SCMs (Fig. 12d, e) with those obtained for hydrated white Portland cement-SCM blends (Fig. 13c, d). Thus, spectral deconvolution approaches are needed to extract information on the degree of SCM reactions.

A first approach is to generate a sub-spectrum for the anhydrous SCM and, in the subsequent analyses of the hydrated samples, assume that its shape will not change during hydration. This assumption corresponds to congruent dissolution of the SCM during hydration. Deconvolutions of good quality have been

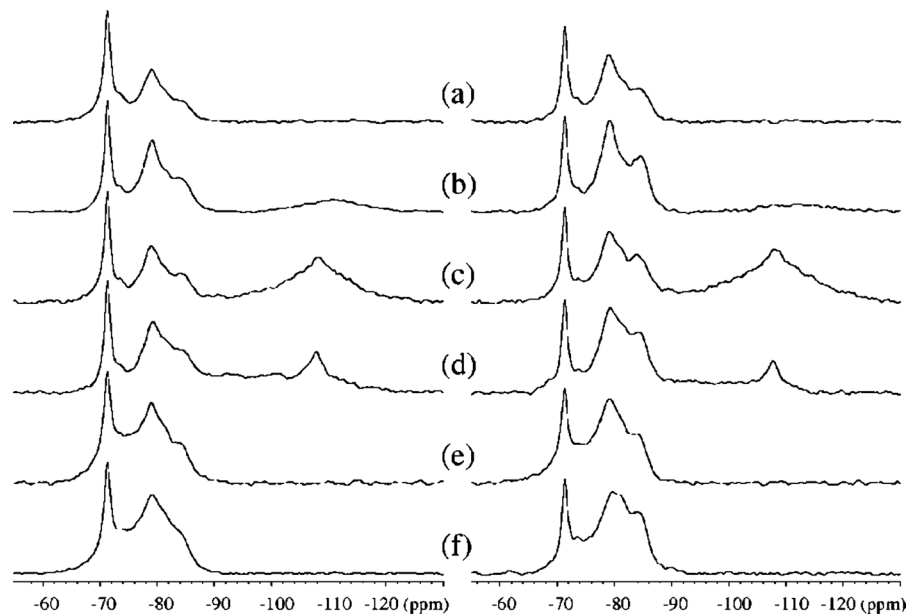
**Fig. 12**  $^{29}\text{Si}$  MAS NMR spectra (9.4 T,  $\nu_R = 12.0$  kHz, *left column*) and  $^{27}\text{Al}$  MAS NMR spectra (14.1 T,  $\nu_R = 13.0$  kHz, *right column*) of the pure anhydrous samples of *a* a white Portland cement (WPC), *b* an ordinary Portland cement, *c* silica fume, *d* a low-iron fly ash, *e* a natural pozzolan, and *f, g* two different slags (S1 and S2). The spectra are not shown on normalised intensity scales. From Poulsen et al. [61]



obtained by this approach for the low-iron fly ash and natural pozzolan in Fig. 13 and for similar studies of Portland cement-metakaolin blends. For Portland cement-slag systems, the overlap of resonances in the  $^{29}\text{Si}$  MAS NMR spectra from the anhydrous and hydrated components become much more severe, and reliable quantification of the SCM reaction may be hard to achieve from deconvolutions of these spectra. For example, the assumption of congruent dissolution of the slag was questioned by Dyson et al. [24] in a  $^{29}\text{Si}$  NMR study of a hydrated Portland cement-slag system (75:25 w/w). In addition to different deconvolution approaches of the  $^{29}\text{Si}$  MAS spectrum for the hydrated slag cement, they also employed selective dissolution of the calcium silicate phases, leaving a residue assigned to unreacted slag. The  $^{29}\text{Si}$  MAS NMR spectrum of this residue deviates from the corresponding spectrum of the anhydrous slag and Dyson et al. [24] concluded that the optimum approach to deconvolute the spectrum of the hydrated cement-slag blend was to use a sub-spectrum for the slag based on the spectrum of the non-dissolved residue, thereby considering effects from incongruent slag dissolution. This approach, and particularly the use of a sub-spectrum for the slag based on the dissolution residue,

was examined in a study of slag reaction in alkali-activated binders by Le Saout et al. [48], who found that the sub-spectrum based on the spectrum of the anhydrous slag gave the most satisfactory results in their deconvolutions. This indicates that the  $^{29}\text{Si}$  MAS NMR spectra of the alkali-activated slags do not give clear evidence for a preferential dissolution of specific  $^{29}\text{Si}$  sites in the slag. This divergence of views almost certainly arises from the fact that leached layers tend to be formed on glasses in the acidic solutions used for selective dissolution, but not in alkaline solutions as found in cement blends [37, 57, 71] and supports the use of sub spectra from the original anhydrous material.

Alternatively, the degree of slag reaction can be derived from  $^{27}\text{Al}$  MAS NMR, using the characteristic centreband resonance from the slag, which will dominate the spectral region for Al in tetrahedral coordination (Skibsted [69]). This approach is illustrated in Fig. 14 and employs  $^{27}\text{Al}$  MAS NMR spectra of weighed samples of the anhydrous slag and the hydrated cement-slag blend. The spectrum of the anhydrous slag is subtracted from the spectrum of the hydrated blend in such a manner that the resonance from the anhydrous slag is removed from the spectrum



**Fig. 13**  $^{29}\text{Si}$  MAS NMR spectra (9.4 T,  $\nu_{\text{R}} = 12.0$  kHz) of cement (WPC)—SCM pastes after 7 days (*left column*) and 28 days (*right column*) of hydration. *a* Pure WPC, *b* 90 wt% WPC + 10 wt% silica fume, *c* 70 wt% WPC + 30 wt% low-

iron fly ash, *d* 70 wt% WPC + 30 wt% natural pozzolan, *e* 60 wt% WPC + 40 wt% slag S1, and *f* 60 wt% WPC + 40 wt% slag S2. From Poulsen et al. [61]

of the partially hydrated material. From the scaling factor of the slag spectrum used in this subtraction and by correction for the water content in the hydrated material, obtained as the loss of ignition, the fraction of unreacted slag, and thereby the degree of slag reaction, can be determined for the hydrated sample. Again, this approach assumes congruent dissolution of the slag during hydration. However, it has been tested for different slag-cement systems and found to give degrees of slag reaction that match well with results from calorimetry and chemical shrinkage for the same samples. Moreover, the same approach has proven useful in the analysis of the degree of glass reaction in hydrated cement-glass blends.

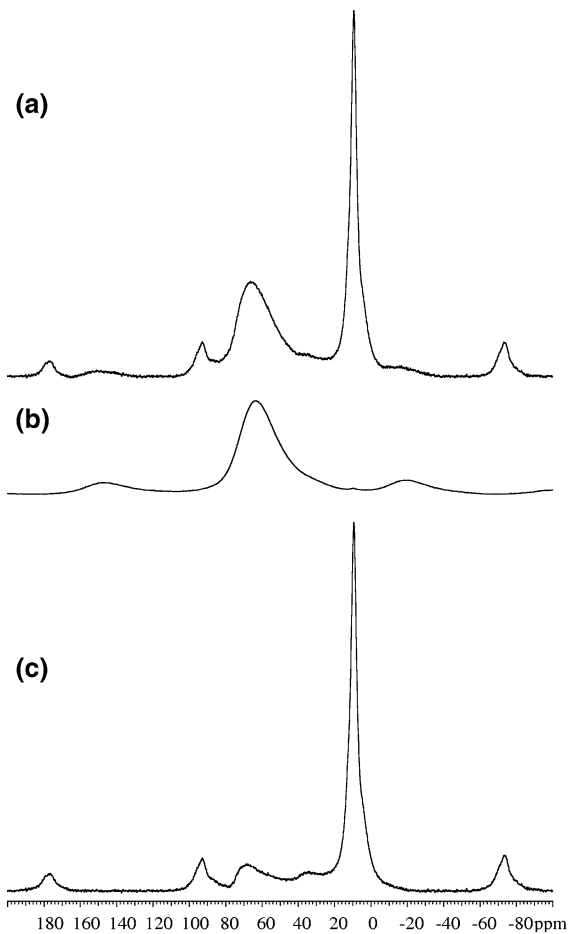
## 2.4 XRD

The conventional view of the use of quantitative diffraction methods in the study of hydrated cements is that XRD coupled with Rietveld analysis can only be used satisfactorily to quantify crystalline phases, or the total amount of amorphous materials if an internal or external standard is used. This approach is not very useful in cementitious blends where both the main hydrate, C–S–H and the SCMs are amorphous. However, recently there has been considerable interest

in looking at whether the quantities of different amorphous materials can be quantified from the broad hump they give in the XRD diffractograms, by the so called partial or no known crystal structure (PONKCS) technique.

The analysis of powder XRD data of hydrating blended cements has been largely limited to: (1) the quantification of the degree of hydration of the crystalline clinker phases, and (2) the formation of crystalline hydration products [3, 66]. Hydrating cements are complex materials consisting of numerous coexisting phases, both residual anhydrous phases and hydration products that can each have variable composition and crystallinity. In a typical hydrating Portland cement at least around 10 different phases can be expected to be present simultaneously, while hydrating blended cements show an additional level of complexity. Therefore, one of the most important problems that needs to be dealt with is the significant overlap of the contributions of the peaks from the various phases. A particular difficulty is to correctly assign the contributions of amorphous or nanocrystalline phases such as blast furnace slag or C–S–H, that appear as diffuse, broad peaks in the XRD data.

New approaches blend a profile summation method with the Rietveld method using the PONKCS

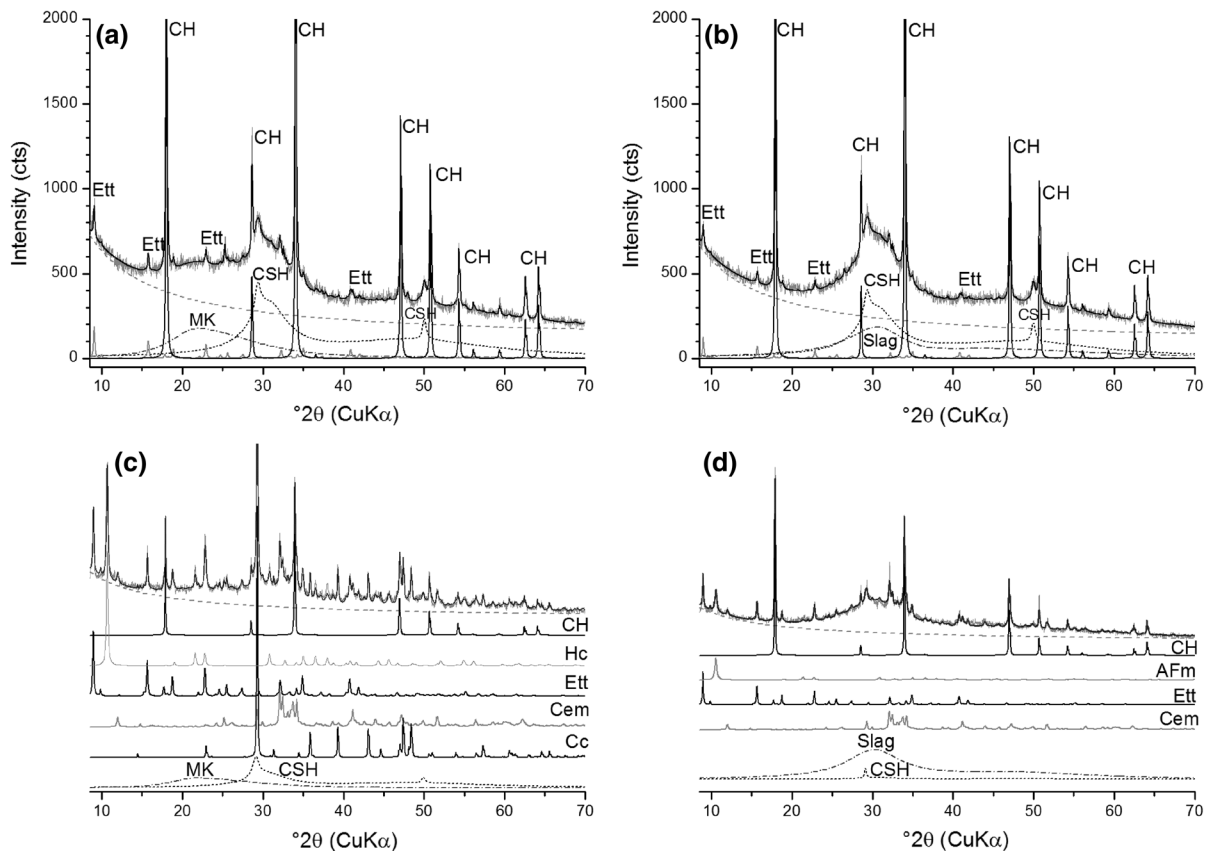


**Fig. 14**  $^{27}\text{Al}$  MAS NMR spectra (14.1 T,  $\nu_{\text{R}} = 13.0$  kHz) of **a** a Portland cement—slag blend (60:40 w/w) hydrated for 24 days, **b** the anhydrous slag (S1) and **c** a difference plot between **(a)** and **(b)** using a scaling factor of 0.22 for the spectrum in **(b)**. From Skibsted [69]

approach [63]. This method takes into account the contribution of a phase that has no or no fully known crystal structure by the assignment of a “phase constant” relating the diffraction signal of the phase to its content. The determination of the phase constant is carried out in a mixture in which the content of the phase is known. In case of SCMs this requires a separate scan of the SCM component for calibration of the technique. The determined phase constant can then be used in combination with a refined scale factor to calculate the phase weight fraction in unknown mixes. However, Inadequate modelling of the amorphous contributions may lead to an important bias in the quantification of overlapping crystalline phases, e.g. C–S–H and alite or belite.

The PONCKS method was recently applied to the quantification of the degree of reaction of metakaolin in alkali activated systems [80], and in the quantification of C–S–H in the early hydration of alite [8]. The precision and accuracy of the PONCKS approach in the quantification of amorphous SCM (blast furnace slag and metakaolin) levels in blended cements was assessed recently in synthetic model mixes [72]. In mixes in which the SCMs were the sole unknown/amorphous components combined with a number of crystalline phases, excellent precision (around 1 wt%) and accuracy (2–3 wt%) of the SCM quantification results were obtained. This analytical performance is similar to the errors for quantitative XRD on the crystalline phases in anhydrous cements [46, 47].

A particular difficulty in hydrated blended cements is the simultaneous presence of an amorphous SCM and the C–S–H phase. The C–S–H contribution will partially (e.g. metakaolin) or entirely (e.g. blast furnace slag) overlap with the SCM signal (Fig. 15), making the appropriate choice and calibration of a “peak model” for the C–S–H contribution essential in obtaining accurate quantification results. Figure 15 shows synthetic mixes of a 7-years hydrated white cement, mainly composed of C–S–H, portlandite, and fixed quantities of metakaolin and blast furnace slag. The C–S–H model was obtained from the hydrated white cement. The quantification results were very close to the mixing proportions (within 1 wt%), demonstrating the reliability of the method for systems containing combinations of well-calibrated amorphous phases. A comparison between the measured and weighed proportions of amorphous SCMs and C–S–H in a variety of predefined mixes is presented in Fig. 16. The very limited scatter around the linear 1:1 relationship is indicative of the potential of the method [72]. The successful application to synthetic systems encourages the use of the PONCKS method in the determination of the degree of reaction of SCMs in blended cements. The experimental data and the decomposition of the calculated pattern for two hydrated blended cements are illustrated in Fig. 15. The quantification approach relied on the measurement of separate patterns of the SCMs and assumed congruent dissolution of the components. The C–S–H pattern and phase constant were adopted from the hydrated white cement. The XRD results for SCM degree of reaction after 3 days of hydration were 11 and 8 %, for the metakaolin and the slag blended



**Fig. 15** XRD scans and analysis of the Rietveld-PONCKS fitting results of (a) a synthetic mix of a 7-years hydrated white Portland cement (70 wt%) and metakaolin (30 wt%), (b) a synthetic mix of a 7-years hydrated white Portland cement (70 wt%) and blast furnace slag (30 wt%), (c) a 3 days hydrated blended cement initially containing 30 wt% metakaolin,

cement, respectively. The results are close to the calculation of the metakaolin degree of reaction by mass balance of 13 % (at 7 days, same system, same metakaolin) [1], and the determination of the slag degree of reaction determined by SEM-BSE-IA of 12 % (at 3 days, same slag, 40 % slag) [44].

The advantages of the PONCKS method are the relatively widespread availability of XRD equipment and the potential general applicability to all SCMs. Using fairly modern equipment with fast detectors, data acquisition times are less than 1 h. In addition, the method can be implemented fairly easily into existing software packages for Rietveld analysis by a skilled operator. The method is therefore likely to find more widespread use, especially because there are in principle no specific limitations regarding the SCM type or composition. However, it should be noted that

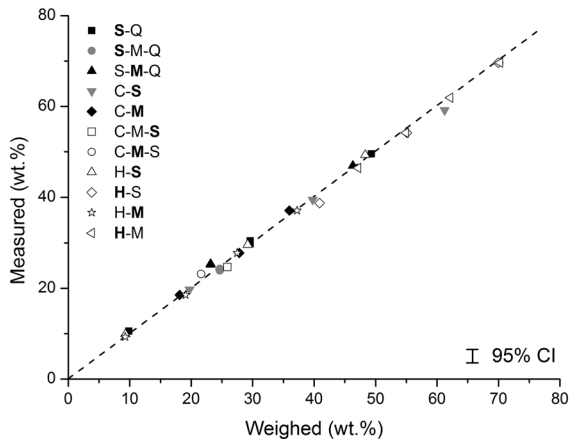
15 wt% limestone and 55 wt% Portland cement, (d) a 3 days hydrated blend of 60 wt% blast furnace slag and 40 wt% Portland. Contributions of ettringite (Ett), portlandite (CH), C–S–H (CSH), metakaolin (MK), blast furnace slag (Slag), hemicarboaluminate (Hc/AFm), and anhydrous cement phases (CEM) are indicated. Adapted from Snellings et al. [72]

the sensitivity and detection limits inherent to the XRD technique constrain the field of application to the study of blended cements with replacement levels higher than 10 %. Below 10 % replacement, the precision of the method is expected to be poor due to the estimated 2–3 wt% error in the SCM quantification. Moreover, detection limits are relatively high for amorphous phases and it is doubtful whether SCM residues below 3–5 wt% are reliably quantifiable. In consequence, the analytical precision will also decrease at high degrees of reaction.

### 3 Indirect methods

Indirect methods rely on measuring the quantity of hydrates formed and then inferring the amount of





**Fig. 16** Cross plot of weighed and measured proportions of slag (S), metakaolin (M), and C–S–H(H) in synthetic mixes with quartz (Q), anhydrous cement (C), and hydrated cement mixes. Adapted from Snellings et al. [72]

SCM reacted based on hypotheses about the hydration reactions. There are several aspects which make such methods complicated and sometimes inaccurate:

1. It is usually necessary to measure or assume a degree of reaction of the clinker phases. This must take into account the acceleration of the reaction of these phases due to the filler effect.
2. A stoichiometry for the reaction of the SCM must be assumed. For example, it is often assumed simplistically that the pozzolanic reaction is simply between calcium hydroxide and the silicate component of the SCM. However, the SCMs may also contain alumina which enters the hydrates, which must be taken into account in the calculations. Changes in the composition of the C–S–H phase must also be considered as detailed below.
3. There is a significant change in the composition of the C–S–H phase between pure Portland cements on the one hand and blended pastes on the other (e.g. [50]). As this phase typically constitutes around half of the final volume of a paste, small errors in the assumed composition of C–S–H will have a very large impact on the assessment of the degree of hydration.

Despite these complications, estimates of the degree of hydration can be obtained by combining information about the different phases in mass/volume balance or thermodynamic modelling approaches. In

such approaches it is very important to give due consideration to the accumulation of errors. Often two values of similar magnitude, each with a significant absolute error, are subtracted so the relative error of the difference is very large. All too often, papers show graphs of results without any error bars, while a basic knowledge of the characterisation techniques involved makes it clear that the differences discussed are well within the experimental error.

### 3.1 Thermogravimetric methods

Many studies try to assess the degree of reaction of SCM from simple measurements of either bound water or calcium hydroxide.

#### 3.1.1 Bound water

The most widely used technique to assess the degree of reaction of plain Portland cements is evaluation of the bound water content based on the weight loss of samples between (typically) 105 °C and 1,000 °C.

Despite the various stoichiometries of the reactions of the various clinker phases, it is usually found that the average values of bound water per gram of reacted material are similar for different Portland cements (0.23–0.25 g/g ignited sample [16, 58]). However, the situation becomes much more complicated when SCMs are used which makes it unrealistic to separate the bound water due to reaction of the SCM from that due to the reaction of the clinker phases, as pointed out by Massazza [53]. Nonetheless, results of Portland and blended cements can be compared as an indication of differences in hydration process between the two types of binder. Differences in the curing temperature from 20 °C will also affect the water content of the C–S–H [28].

A further problem is the reference state for the material. Most studies start from materials which have been oven dried at 105 °C, assuming that all the evaporable water is driven off at temperatures lower than 105 °C [13, 42, 76, 79]. However, some researchers claim that adsorbed (evaporable) water still can be lost between temperatures of 105 and 130 °C or even 150 °C [26, 45, 54]. On the other hand, it is also clear that most of the cement hydrates, particularly C–S–H and ettringite, can lose part of their chemically combined water below 105 °C (e.g. [75], Baquerizo et al. [5]).

The mass loss assumed to come from the chemically bound water ( $w_b$ ) of the CH, C–S–H and other hydrates should also be corrected for the mass loss due to decarbonation (around 650 °C), as pointed out by Pane and Hansen [58]. For this reason it is certainly better to estimate the bound water content from a classical thermogravimetric experiment (continuous measurement of weight under constant heating rate) rather than simply by the difference in weight between 105 and 1,000 °C.

Pane and Hansen proposed a method based on the proportion of bound water at time  $t$  ( $w_{b,t}$ ) relative to the bound water at infinite time. To estimate  $w_{b,\infty}$  experimental data of  $w_b$  as a function of time, was fitted by a three parameter equation [1] (the parameters  $\tau$  and  $a$  respectively control the intercept and curvature of the plot in the logarithmic scale). The ratio of the bound water content at a certain time  $t$  [ $w_b(t)$ ] to the ultimate bound water content was proposed to be an estimate of the overall reaction degree of Portland cement, and was proposed also to be applicable to blended systems [58]. This method implicitly assumes that ultimate bound water content ( $w_{b,\infty}$ ) correspond to 100 % reaction.

$$w_b = w_{b,\infty} \cdot \exp\left[-\left(\frac{\tau}{t}\right)^a\right] \quad (1)$$

Based on this work, Gruyaert [34] calculated the overall degree of reaction of Portland pastes and pastes with slag-to-binder ratios of 0.5 and 0.85. The estimated value of  $w_{b,\infty}$  were 22.1 g/100 g binder for Portland pastes. While the value of  $w_{b,\infty}$  for pastes with a slag-to-binder ratio of 50 % (22.4 %) was similar to the value for Portland paste, but a sharp decline (11.4 %) was recorded for pastes with a slag-to-binder ratio of 0.85. However, it is known that the degree of reaction of slag decreases significantly for blends with high slag proportions [14]. It is clear that the “ultimate” reaction degree in these expressions is in fact the maximum possible reaction for the binders in the given combination, which by no means implies that each binder has fully reacted. While in Portland cements the high degree of reaction after a few weeks or months allows the estimation of an “ultimate” bound water content ( $w_{b,\infty}$ ) or heat ( $Q_\infty$ ), in fly ash or slag blended systems this is a relative value as SCMs, especially fly ashes, may only have reacted partially even after a year or longer. Furthermore, the degree of

reaction calculated does not distinguish between the reaction of the SCM and clinker component. For these reasons the value of such approaches seems limited.

### 3.1.2 Portlandite consumption

When CH decomposes (between 410 and 480 °C) to CaO and H<sub>2</sub>O, a mass loss ( $WL_{CH}$ ) is recorded due to the loss of water. The weight of portlandite (CH) can be calculated from this mass loss taking into account the molecular mass of water in the portlandite formula according to equation [2]

$$CH = WL_{CH} \cdot \frac{MW_{CH}}{MW_{H_2O}} = WL_{CH} \cdot \frac{74}{18} \quad (2)$$

The pozzolanic reactions of fly ash or silica fume are often followed via the decrease of the amount of portlandite in the mixture (e.g. [2, 15, 58]). This method is well suited to assess on a comparative basis the increasing reaction of the SCM with time.

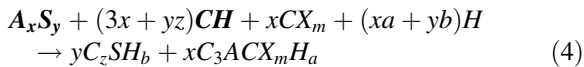
To quantify the reaction of fly ash, SF and BFS, Pane and Hansen [58] developed a method based again on extrapolation of the amount of portlandite versus bound water to infinite time. For a given bound water content ( $w_b$ ) the difference between the water loss due to portlandite in the blend [ $CH_{blend}(w_b)$ ] and that in the reference plain Portland system ( $CH_{PC}$ ) divided by the difference between the two at infinity (Eq. 3) was assumed to be proportional to the degree of reaction of the SCM:

$$r_S(w_b(t)) = \frac{CH_{PC}(w_b(t)) - CH_{blend}(w_b(t))}{CH_{PC}(w_b(\infty)) - CH_{blend}(w_b(\infty))} \quad (3)$$

However, the reliability of quantitative determinations of the fraction of SCM reacted are questionable as the reaction of the clinker might be accelerated and enhanced due to the filler effect. During the first days of hydration more portlandite (proportional to the clinker content) may be observed in a Portland cement—fly ash paste than in a pure Portland cement paste. Changes in C–S–H composition are another major source of error as discussed below.

Rather than fitting the reaction kinetics and assuming complete reaction at infinity a direct calculation of the amount of silica and/or alumina provided by the reaction of an SCM can be calculated from the portlandite consumption, based on the stoichiometry

of the pozzolanic reaction, as generalised in equation [4]:



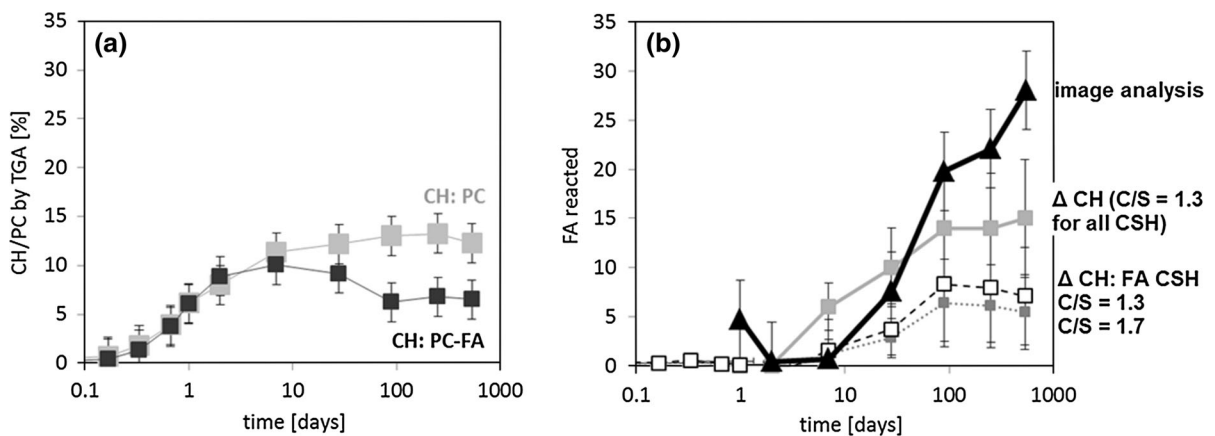
where X stands for a mono- or divalent anion group that can be incorporated into the AFm structure, i.e. sulfate, carbonate, hydroxide, chloride. Here it is necessary to know the alumina to silica ratio in the reacting SCM ( $x$  and  $y$ ) and the composition of the C–S–H formed ( $z$ ). The uptake of alumina in the C–S–H is ignored in Eq. 4 for the sake of clarity but may also be taken into account. Antoni et al. [1] used such a mass balance approach to estimate the degree of reaction of metakaolin based on the portlandite consumption. Metakaolin is a relatively easy example because the ratio of alumina to silica (=1) is well known. The degree of SCM reaction is calculated from the difference between the portlandite present in an equivalent quartz-containing reference paste (to take account of the filler effect) and in the SCM blend. One of the main difficulties associated with such mass balance calculations is the variation in composition of the C–(A–)S–H with SCM addition, as mentioned above and further detailed below.

The presence of an SCM leads to a decrease of the Ca/Si ratio of the C–S–H even if portlandite is still present (e.g. [1, 19, 50]). This indicates that some calcium participating in the reaction of the SCM comes from the C–S–H, and this will result in a serious underestimation of the degree of reaction of the SCM

if only the total CH consumption is considered. Figure 17 shows how different assumptions regarding the stoichiometry of reaction affects the calculation of the amount of fly ash reacted in the study Deschner et al. [19]. In the presence of alumina-rich SCMs such as metakaolin or fly ash, an increase in alumina uptake in the C–S–H is also observed [1, 19]. Beside the changes in the C–S–H composition, its variability may also increase [19], making the determination of the appropriate Ca/Si and Al/Si ratios difficult. Nevertheless, EDS plots of the atomic ratio of Al/Ca versus Si/Ca have been used successfully to determine the composition of the C–A–S–H gel for the calculations (e.g. [1]).

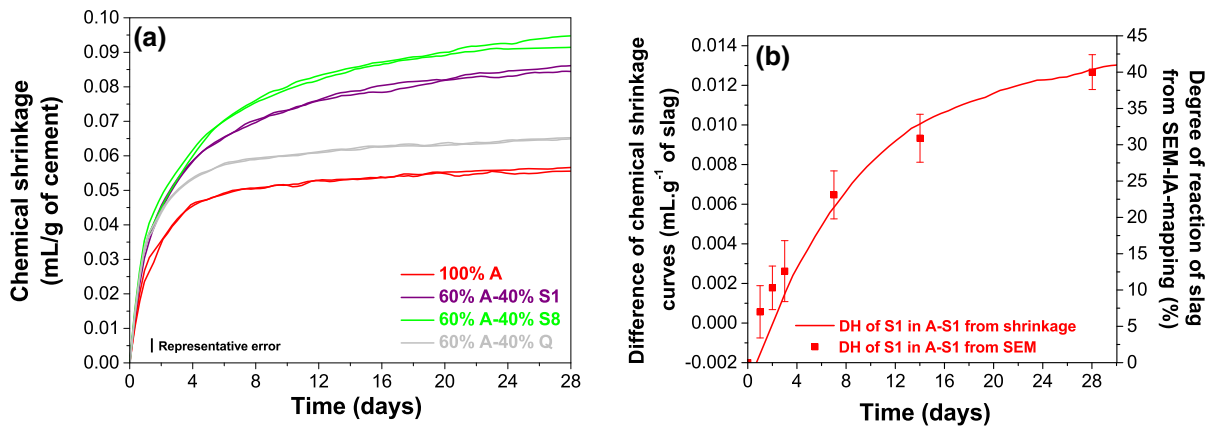
To summarise, such calculations can give correct trends, but are associated with a number of errors:

- Neglecting the filler effect. This may be corrected if comparison is made with a mixture in which the same substitution of the clinker component is made with quartz filler, although even here errors may arise because of differences in particle size distribution of quartz and SCM, use of an impure quartz with some reactive component, hydration at temperatures in excess of 80 °C where quartz becomes thermally reactive [74], and other discrepancies.
- Relatively small changes in the portlandite content can be related to a significant reaction of fly ash or metakaolin, as shown in Fig. 18. As the degree of reaction of the SCM is calculated from a relatively small measured difference in the portlandite



**Fig. 17** **a** Portlandite (CH) content ( $\pm 2\%$ ) in PC and a 50 % PC–50 % fly ash paste, and **b** degree of fly ash reaction obtained by image analysis and by mass balance calculation based on the consumption of CH, assuming (i) that the Ca/Si

ratio of all C–S–H is reduced to 1.3, or (ii) that only the CH reacts with the fly ash, yielding C–S–H with Ca/Si ratios of either 1.3 or 1.7. Calculated based on data from Deschner et al. [19]



**Fig. 18** Evolution of **a** chemical shrinkage and **b** chemical shrinkage calibrated with SEM-BSE-IA-mapping. From Kocaba et al. [44]

content, a measurement error of  $\pm 2$  g/100 g can lead to a relative error of  $\pm 50$  % in the degree of SCM reaction obtained.

- C–S–H composition, one of the determinant factors in the calculation, can be variable and difficult to determine accurately.
- Traditionally the degree of reaction is assessed assuming that the  $\text{SiO}_2$  from the fly ash or silica fume reacts exclusively with portlandite to form C–S–H, which largely underestimates the degree of SCM reaction as shown in Fig. 17. If a reduction in the C/S ratio of all C–S–H is considered, more realistic results can be obtained.
- The formation of other phases, e.g. hemicarbonate or strätlingite, can strongly affect the portlandite consumption.

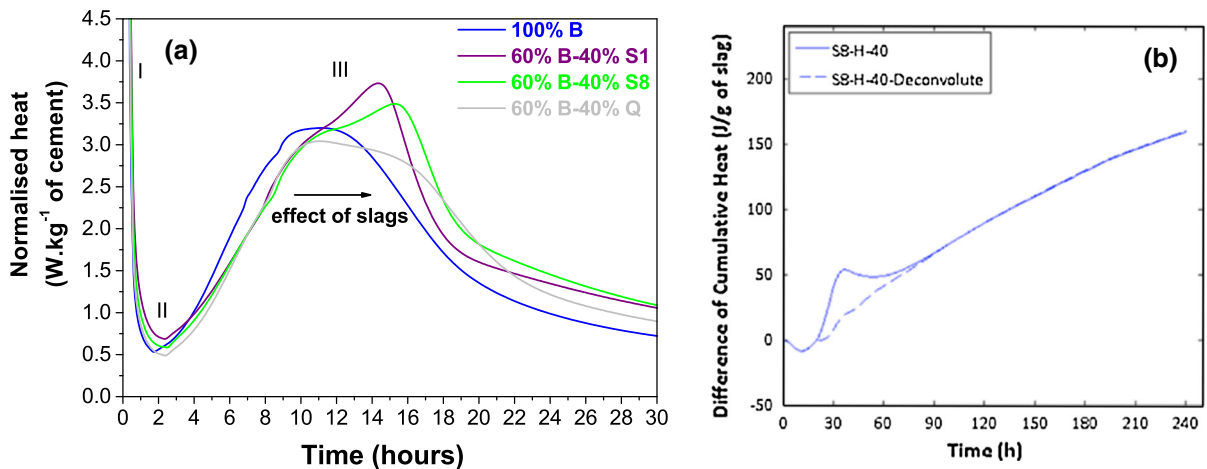
### 3.2 Calorimetry and chemical shrinkage

The overall measurement of the reaction by calorimetry or chemical shrinkage lies somewhere between the direct and indirect approaches. The basis of both methodologies is to compare the hydration of blended cement containing ground clinker (plus calcium sulfate) plus SCM with that of the same Portland cement component (i.e. ground clinker plus calcium sulfate) with the SCM replaced by an inert filler, usually quartz of similar particle size. It is important to make the comparison with the inert filler blend rather than the pure Portland cement to take into account the impact of the filler on the rate of reaction of the clinker

component, as noted for the portlandite consumption method above. This method was described in detail for slag cements in Kocaba et al. [44] and is illustrated in Fig. 18.

Gruyaert [34] also tried to apply this method, but by making a comparison between the blends containing slag and the plain Portland cement mix (i.e. neglecting the filler effect). The curves were normalised by the Portland cement content, but the discrepancies in the early part of the reaction, where the slag was not reacting, indicated the impact of the filler effect. They suggested the use of a fitting factor to bring the early reaction parts into alignment to account for this filler effect.

As seen in Kocaba et al. [44], the excess of heat (or chemical shrinkage) starting after 1 day for the blend containing slag can be related to the reaction of the slag. The main problem associated with this method is that it is difficult to know how the heat from the reaction of the slag relates to the amount of slag reacted. A value of  $460 \text{ J g}^{-1}$  for slag can be found in the literature [40], but, it seems [41] this was derived from the adiabatic heat rise in the first day, when the degree of reaction of slag is negligible and in fact describes the filler effect of slag on the hydration of cement. Some old papers [31, 32] suggest to use the solubilities of hydroxides which form hydrates of slag to calculate the enthalpy of reaction of slag, but the values obtained by this method by Kocaba et al (2011) were too high to be reasonable. To obtain calibration values for the enthalpy of reaction of slags, the difference curve from calorimetry can be compared to the values of degree of reaction from image analysis



**Fig. 19** **a** Impact of slag on aluminate reaction using isothermal calorimetry (shoulder peak after main C3S peak), from Kocaba [43], **b** impact of this aluminate reaction on difference of cumulative heat; from Myers et al. [55]

(Fig. 18). In the work of Kocaba et al. (2011) values of 400–500 J/g were obtained, but there is a large error due mainly to the lack of precision of the image analysis measurements.

Another issue with the method is that the SCM and filler often have different effects on the kinetics of the reaction of the aluminate phase, usually seen as a second or shoulder peak after the maximum of the main heat evolution peak from the reaction of the silicates, Fig. 19a. This leads to the bump in the difference curve seen in Fig. 19b. However, Myers et al. [55] found that this bump did not impact the result calculated at long times.

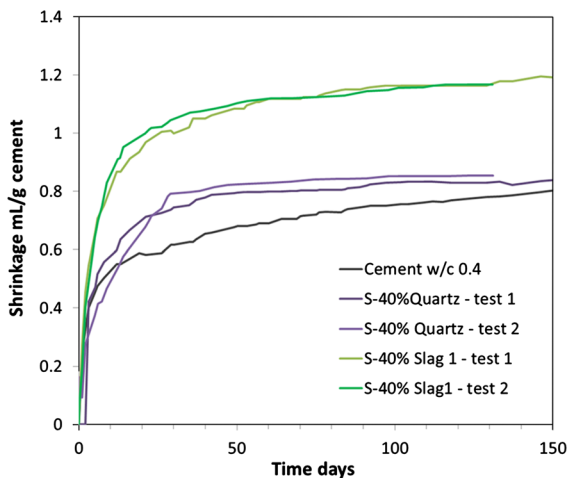
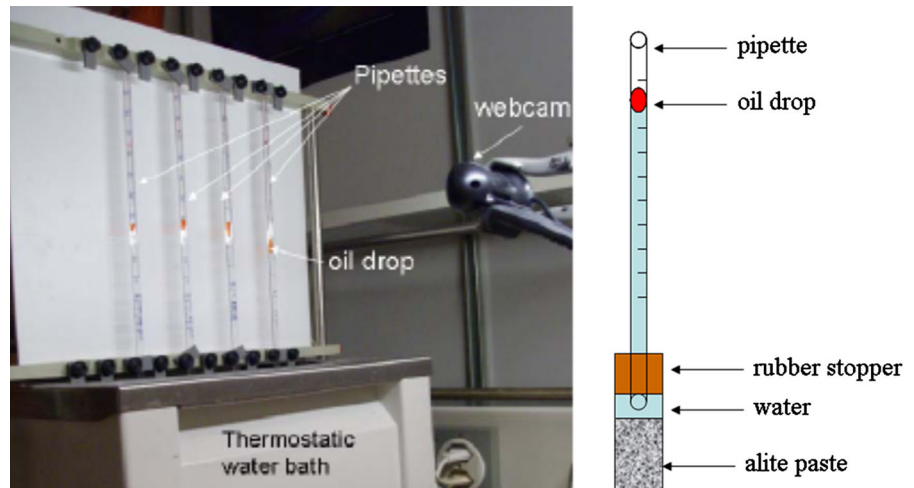
The degree of reaction of a rapidly reacting SCM such as slag, metakaolin or silica fume can certainly be assessed, at least in a comparative manner, by this method. However, more slowly reacting SCMs such as fly ash do not give a large enough heat output up to 28 days for this measurement to be used. The key limitation of calorimetry is that the signal measured is the rate of heat evolution, which is then integrated to give the cumulative heat flow. After a few days the rate signal is very low, and thus a small absolute error in the rate, due to instability of the baseline or inaccurate calibration will lead to a large cumulative errors.

Chemical shrinkage should be a more accurate method to measure reactions over longer time scales,

as the output of this method is directly the cumulative, or total, value rather than a rate. Nevertheless there are many experimental difficulties related to obtaining accurate measurements for chemical shrinkage—including sample thickness, temperature stability, and leakages [17]. The method is illustrated in Fig. 20, and the method, based on Geiker [29] is standardised as ASTM C1608. A small amount of paste is placed at the bottom of a small bottle, which is then completely filled with water. The bottle is stoppered with a pipette through the stopper, and water is added so it comes most of the way up the pipette. The assemblage is then placed in a thermostatic bath. A small amount of coloured oil is placed on top of the water in the pipette to prevent evaporation and enable observation. As the paste hydrates and the overall volume decreases [ $V_{\text{hyd}} < (V_{\text{anh}} + V_{\text{H}_2\text{O}})$ ], water is drawn into the paste and the level in the pipette descends. The coloured oil allows the level to be recorded automatically by a webcam. Up to 20 or so testing stations can be constructed for little more than the cost of a water bath. Methods based on continuous weighing also exist although these can usually only measure one sample at a time, which together with the cost of an accurate balance, makes the methods more expensive.

Figure 21 shows chemical shrinkage data for slag blends (including repetitions) collected over 4 months by Berodier [9, 10]. This illustrates that reasonably reproducible measurements can be obtained. As with

**Fig. 20** Chemical shrinkage method by water absorption



**Fig. 21** Chemical shrinkage measurements, from Berodier [9, 10]

calorimetry, the main difficulty of the chemical shrinkage methods is related to the calibration, i.e. how to relate the extra chemical shrinkage to the degree of reaction. Here the problem is similar to that discussed for bound water measurements, namely that the exact stoichiometry and specific volumes of the hydrates formed, particularly C–S–H, are not well known. More work is needed here, but the method does give a good, inexpensive and non-labour intensive method to follow the reaction of SCMs on a comparative basis.

## 4 Recommendations for individual SCMs

In this section we try to summarise the suitability of the different methods discussed in this paper for the different types of SCMs. In many cases these remarks are based on our knowledge of the physical principles involved as not all methods have been systematically studied on each SCM.

### 4.1 Slag

Method	Rating	Comments
Selective dissolution	Poor	The SCM for which selective dissolution has been most widely used. Nevertheless, too many problems have been identified for this to be recommended as a reliable method of measuring degree of hydration  The method can work better in “pure” systems, e.g. alkali activated or supersulfated slags when no clinker is present. It should be checked on pure phases separately for re-precipitation. Estimated accuracy around $\pm 10\%$ at best

Method	Rating	Comments
Image analysis	Good	Homogeneity of slag means this method can work well, especially if combined with chemical mapping to avoid the problem of overlapping grey levels with portlandite. However, a sufficient number of images must be analysed and overall the method is very time consuming with still a fairly low precision. Tends to overestimate degree of hydration at early ages due to the problem of resolving fine particles. Estimated accuracy around $\pm 5\%$
NMR	Good	Probably most difficult of the common SCMs to quantify by $^{29}\text{Si}$ NMR due to overlap of peak with clinker phases and hydration products. $^{27}\text{Al}$ MAS NMR, performed at high magnetic field ( $>11.7\text{ T}$ ), is much better than $^{29}\text{Si}$ NMR due to the clear detection of Al in fourfold coordination from the slag
XRD	promising	PONKCS approach is promising; more work is needed to check reproducibility of results. Possible interference by C–S–H signal, appropriate C–S–H model needed. Estimated precision on slag quantification: $\pm 3\text{--}4\text{ wt}\%$
Calorimetry/chemical shrinkage	Good	As reaction starts around 1–2 days good data can be obtained on a comparable basis. Fast and reliable technique although translating heat evolution to absolute degree of hydration is still an outstanding issue  The impact of the filler effect may change with the stage of hydration
Mass balance	poor	Not recommended as CH consumption is so low and C–S–H composition is significantly changed, so very high errors

*Recommendation for slag* Image analysis, NMR and calorimetry/chemical shrinkage seem to be useful methods as they can be reasonably accurate.

#### 4.2 Fly ash

Due to heterogeneity probably the most difficult SCM to quantify.

Method	Rating	Comments
Selective dissolution	Poor	Same issues as for slag
Image analysis	Poor but improvements possible	Very difficult, maybe OK for some fly ashes, but in general not recommended. New methods with quantitative EDS mapping to segment fly ash particles from hydrated matrix and to follow the reaction of glass groups of different composition separately look very promising, but time consuming. Sources with a high proportion of fine particles will have higher errors due to lower limit of resolution (1–2 $\mu\text{m}$ )
NMR	Good if low iron. not applicable otherwise	Limited to fly ashes with low iron contents. Should give reasonable results if heterogeneity of glass composition is not too high. Very time consuming and not widely available. Because of this very few studies are reported. The few existing studies look promising
XRD	Not tried	Different reaction rates of different glasses in compositionally heterogeneous fly ashes will need to be taken into account, and may strongly reduce the accuracy of the profile decomposition method

Method	Rating	Comments
Calorimetry/ chemical shrinkage	Poor	Very low reaction before 28 days means calorimetry method is not practical. There is a lack of data to assess the usefulness of long term chemical shrinkage measurements
Mass balance	Moderate	If acceleration of hydration of clinker phases and change in composition of C–S–H are taken into account, this is probably the least bad method

*Recommendation for fly ash* NMR seems to be reliable but limited to fly ashes with low iron content. New method [23] based on full chemical mapping and image analysis looks promising. Mass balance is a good option if necessary cautions are taken into account.

#### 4.3 Silica fume

Challenges are small particle size and low level of additions typically used, which increases relative errors. Poor dispersion makes an extra problem in pastes.

Method	Rating	Comments
Selective dissolution	Not recommended	No known studies, very small and reactive particles unlikely to give viable results
Image analysis	Not possible	Totally impossible to resolve small particles
NMR	Very good	Homogeneity and composition of glass means that the peak is well separated and can be quantified
XRD	Difficult	Limited due to low addition
Calorimetry/ chemical shrinkage	Reasonable	Works well as reaction starts early. Although the difference is small, in the usual range of additions, it has been found to correlate well with NMR

Method	Rating	Comments
Mass balance	Difficult	Need to have good estimate for average composition of C–S–H made on polished samples. Measurements must take into account the intermixing of silica fume, so in practice rather difficult to obtain

*Recommendation for silica fume* NMR is certainly the best technique. If this is not available rough estimates can be obtained from calorimetry or mass balance.

#### 4.4 Metakaolin, calcined clay

Method	Rating	Comments
Selective dissolution	Not recommended	No validated techniques available for this SCM
Image analysis	Not possible	Very fine particles make image analysis approach impossible
NMR	Good	Both $^{29}\text{Si}$ and $^{27}\text{Al}$ NMR can give good results
XRD	Good	Good precision obtainable in PONKCS method as the peak profiles of metakaolin and other calcined clays do not overlap with C–S–H hydration products, compares well with calorimetry heat flow results
Calorimetry/ chemical shrinkage	Good	As reaction starts rather early good data can be obtained on a comparable basis. Fast and reliable technique although translating heat evolution to absolute degree of hydration is still an outstanding issue
Mass balance	Difficult	Complicated as metakaolin provides both silica and alumina into the hydrating system, so stoichiometry of the reaction needs to be assumed. Difficult to estimate C–S–H composition in finely intermixed sample



*Recommendation for metakaolin, calcined clay* NMR is good, but not universally available. PONCKS method with XRD is very promising. Calorimetry is good on a comparative basis. Mass balance can give a reasonable estimate but requires further development.

#### 4.5 Natural pozzolans

Method	Rating	Comments
Selective dissolution	Not recommended	No known experiences
Image analysis	Challenging	Very variable mineralogy will make this very difficult as for fly ash. No known systematic studies
NMR	Reasonable in certain cases	Limited experience
XRD	Not tried but promising	Depends on material heterogeneity. Works very well for crystalline pozzolans such as zeolites. Expected to work well for natural pozzolans containing an amorphous reactive phase
Calorimetry/chemical shrinkage	Poor	No experience, but in general the low levels of reactivity will mean this is impractical
Mass balance	Poor	No known experience. Variable mineralogy will make stoichiometric assumptions of reaction difficult

#### 4.6 Limestone

Low levels of reaction mean that the relative error of estimating the degree of hydration will generally be high.

Method	Rating	Comments
Selective dissolution	No known methods	
Image analysis	Not possible	Very fine particles make image analysis approaches impossible
NMR	Poor	<sup>13</sup> C NMR is a time-consuming (days measurement time) and less suitable method due to precision [67]

Method	Rating	Comments
XRD	Good	Care needed to minimise preferential orientation, but can give reasonable accuracy. Production of hydrates (mass balance) is much more reliable than consumption of calcite
TGA	Poor	Reasonable technique but difficult to quantify the low levels of reaction in practice. Carbonation of samples can give a major interference
Calorimetry/chemical shrinkage	No	Very low enthalpy of reactions means signal is too low
Mass balance	Reasonable	Quantification of mono (hemi) carbonate can give a reasonable estimate

*Recommendation for limestone* Comparison of measurements of calcite reacted (by XRD or TGA) and amount of mono (or hemi) carbonate formed gives a reasonable estimate.

## 5 Concluding remarks

From this review it is clear that measuring the degree of reaction of SCMs remains challenging. Nevertheless, progress has been made in recent years to offer alternatives to the traditional selective dissolution methods. Unfortunately some of these, such as image analysis and EDS mapping in the SEM and NMR, depend on access to expensive equipment and are time consuming. For SCMs that react relatively quickly (e.g. slag, calcined clay) the methods based on calorimetry and chemical shrinkage seem promising on a comparative basis, although the issue of calibration remains. The possibility to quantify amorphous phase by XRD is also extremely promising as this is a widely available and rapid technique which can at the same time give a wealth of additional information on the phases formed.

A major problem in this review has been trying to compare methods applied to systems with different SCMs, even if of the same type (e.g. fly ash), blended with different clinkers, and produced in different labs with different casting and storage methods. It is

important to realise that all methods have an intrinsic uncertainty and a proper consideration of this is essential. The best estimate of likely errors is to make separate measurements on different, but nominally similar samples (same composition, curing time etc.). To address this point the WG2 of the RILEM TC 238-SCM has launched a round-robin study where samples from the same mixes, made in the same laboratory will be measured with different techniques in different laboratories. It is hoped that this study will give a better idea of the comparative accuracy of the different techniques.

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