Determination of the degree of reaction of fly ash in blended cement pastes

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Abstract

This paper gives a review over methods to determine the degree of reaction for supplementary cementitious materials (SCMs) with focus on Portland cement - fly ash blends only and summarizes and highlights the most important findings which are detailed in a parallel paper published in Materials and Structures.
Determination of the extent of the reaction of SCMs in mixtures is complicated for several reasons: (1) the physical presence of SCMs affects the rate and extent of the reaction of the ground clinker component – the so called "filler effect"; (2) SCMs are usually amorphous with complex and varied mineralogy which make them difficult to quantify by many classical techniques such as X-ray diffraction; (3) the rate of reaction of SCMs in a cement blend may be quite different from its rate of reaction in systems containing simply alkali or lime.
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 – image analysis and EDS mapping in the scanning electron microscope, and NMR - depend on access to expensive equipment and are time consuming. With regard to fly ashes, NMR seems to be reliable but limited to fly ash with low iron content. New methods with quantitative EDS mapping to segment fly ash particles from the hydrated matrix and to follow the reaction of glass groups of disparate 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 μm). Whereas for SCMs which react relatively fast (e.g. slag, calcined clay) the methods based on calorimetry and chemical shrinkage seem promising on a comparative basis, the very low reaction degree of fly ashes before 28 days means that the calorimetry method is not practical. There is a lack of data to assess the usefulness of long term chemical shrinkage measurements. The possibility to quantify the amorphous phase by XRD is 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. However, the different reaction rates of different glasses in compositionally heterogeneous fly ashes will need to be accounted for and may strongly reduce the accuracy of the profile decomposition method.
This paper is the work of working group 2 of the RILEM TC 238-SCM "Hydration and microstructure of concrete with supplementary cementitious materials".

Originality

Systematic studies comparing different methods to determine reaction degrees of SCMs are absent in literature. This paper discusses the different techniques, how they operate and the advantages and limitations along with more details related to the application on fly ash. Perspectives for future work are also provided.

***Keywords**: supplementary cementitious material; reaction degree; fly ash; quantitative analysis; filler effect*

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1. Introduction

The different methods which have been used to assess the degree of reaction of various SCMs 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 back-calculate the degree of reaction of the SCM based on hypotheses about the reaction products of the SCMs. The direct methods include selective dissolution, Back Scatter Electron (BSE) image analysis, Nuclear Magnetic Resonance (NMR) and X-Ray Diffraction (XRD) in combination with special Rietveld refinement techniques (PONKCS - Partial or No Known Crystal Structure). Indirect methods include thermogravimetric methods, calorimetry, and chemical shrinkage. 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. The filler effect has two components: (1) The substitution of clinker by an SCM at the same water to binder ratio implies a dilution effect and a higher effective water to cement ratio. 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; (2) The surfaces of the SCM may act as nucleation sites for hydrates. 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. A correction may be made for the filler effect 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 between quartz and the SCM studied, use of impure quartz with some reactive component, or hydration at temperatures in excess of 80°C where quartz becomes thermally reactive (Taylor, 1977).

This paper is the work of working group 2 of the RILEM TC 238-SCM “Hydration and microstructure of concrete with supplementary cementitious materials”. For a full overview of methods to determine degree of reaction of various SCMs, including slag, fly ash, silica fume, and general principles for metakaolin, calcined clay, natural pozzolans, and limestone, reference is made to Scrivener et al. (2015). The current overview is part of the former study and provides a summary for blends with fly ash only.

2. Direct methods

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. However, errors may be introduced if significant amounts of clinker and hydrate phases remain after dissolution, as was shown in studies of residues by X-ray diffraction and SEM (Luke and Glasser, 1987; Ben Haha et al., 2010; Gruskovnjak et al., 2011).

2.1.1. Salicylic acid methods for fly ash

As a solvent, 5 g salicylic acid and 4.2 ml hydrochloric acid is applied, diluted to 100 ml with methanol (DIN 2007). 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. Therefore, correction for sulfates is necessary (Vollpracht and Brameshuber, 2010).

2.1.2. Picric acid methods for fly ash

Another method that can potentially work well with fly ashes is based on picric acid. However, some compounds and reaction products of picric acid can pose a severe explosion hazard. Ohsawa et al. (1985) considered the technique with picric acid-methanol and water the best compromise between dissolving the hydration product enough, but not too much of the fly ash. Baert (2009) subjected different types of cement and fly ash separately to the selective dissolution and observed that the solution dissolved more than 90% of the Portland cement and typically 6-13% of the fly ashes.

Figure 1 shows the results obtained by Baert (2009) for the reaction of fly ash in a paste with fly ash / binder ratio 0.50 and water/binder ratio 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. After 2 years, the measured reaction degree $\alpha_{\text{fly ash}}$ was 28%. The calcium hydroxide consumed by the fly ash, calculated based on TGA measurements (see 6.1.2), is also plotted versus time in figure 1. For C/S = 1.7 a value of 0.7 would be expected.

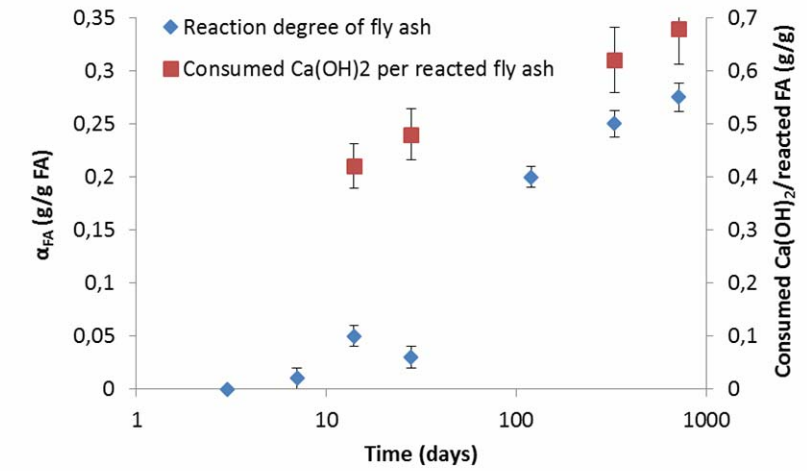

Figure 1: Reaction degree of fly ash in paste with 50% OPC, 50% fly ash and water-to-binder ratio of 0.40; corresponding consumption of calcium hydroxide determined by TGA. Based on Baert (2009).

2.1.2. 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. In a study of Ben Haha et al. (2010) it was observed that 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 left a large fraction of the Portland cement undissolved. Table 1 illustrates that for a higher dissolution degree for the raw fly ash (lower mass of the residue), a higher range between the minimum and maximum reaction degrees is obtained. This implies that one procedure may be more accurate than another in accordance with the composition of the fly ash. When using the salicylic acid + HCl method, a high-calcium fly ash (20.7 % CaO content) showed a residue of 79%, in contrast with a residue of 98% for a low-calcium fly ash (0.06% CaO), making the first less suitable than the second to be studied with this selective dissolution method (Villagran, 2015 – unpublished results).

Table 1: Results of selective dissolution: mass of the residue as % of the initial mass, and degree of fly ash reaction for a mix with 80% OPC and 20% fly ash after 3 months. Min: corrected for initial reaction of the fly ash; max: uncorrected. From Ben Haha et al. (2010).

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
fly ash reaction minimum	32	15	20	3	17
fly ash reaction maximum	43	21	27	4	21

Ben Haha et al. (2010) also compared the reaction degree of fly ash in blended cement determined by selective dissolution (using EDTA NaOH) and by image analysis (IA). 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. The percentage of reacted fly ash determined by selective dissolution was generally lower than the values obtained by image analysis. This could be due to a significant amount of hydrates remaining in the residue of selective dissolution, but also to inaccuracy of the image analysis due to the heterogeneity and the small particle size of the fly ash (small particles are not detected and therefore counted as reacted).

3. 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, 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 (Scrivener et al., 1987; Scrivener et al., 2004). Sources with a high proportion of fine particles will have higher errors due to lower limit of resolution (1-2 μm).

The number of images needed to achieve a reasonably accurate measurement (say +/- 5%) may vary between 10-20 and 100-200 depending on the nature of the SCM, the replacement level, the magnification of the images and the heterogeneity of the sample. Due to the heterogeneous composition of fly ash, it contains phases with many and varied grey levels, with overlap with hydrates or clinker phases. Nevertheless, in the samples studied by Ben Haha et al. (2010) and Deschner et al. (2013) it was possible to identify a peak in the histogram of the samples that could be attributed to the major part of unreacted fly ash (FA in Figure 2). Additionally, the histogram shows peaks correlating to porosity, hydrate phases, clinker and high iron content components of the fly ash.

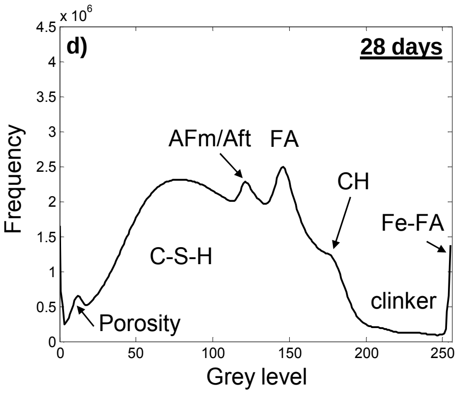

Figure 2: Representative histogram of BSE images of Portland-fly ash blend after 28 days of hydration. From Deschner et al. (2013).

A combination of grey level thresholding and different morphological filters can be applied to distinguish between the unreacted fly ash and the hydrated phases, as described in more detail in Ben Haha et al. (2010) and Deschner et al. (2013). Recently Durdzinski et al. (2015) proposed a new method to analyse fly ash in blended materials based on full chemical mapping. Frequency determination of the main components SiO_2, Al_2O_3, and CaO 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. Na_2O, K_2O, MgO). This method can then be used to assess the degree of hydration for each of the different categories.

To summarise, the BSE image analysis method is in general not recommended for fly ash blends. Nevertheless, new methods with quantitative EDS mapping look very promising, but time consuming.

4. NMR

Solid-state magic-angle-spinning (MAS) NMR spectroscopy has been used to follow the hydration of the Portland cement along with reaction of 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 (Skibsted et al., 2007). 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}Si or ^{27}Al as structural NMR-spin probes. A critical factor for all NMR experiments is the content of paramagnetic ions in the material. In ^{29}Si MAS NMR of Portland cements it was found that quantitative results can be achieved for cements with a Fe_2O_3 content below 5 wt.% Fe_2O_3 (Poulsen et al., 2009). This implies that NMR is limited to fly ashes with low iron contents. Spectral deconvolution approaches are needed to extract information on the degree of SCM reactions (Figure 2). These should give reasonable results if the heterogeneity of the glass composition is not too high.

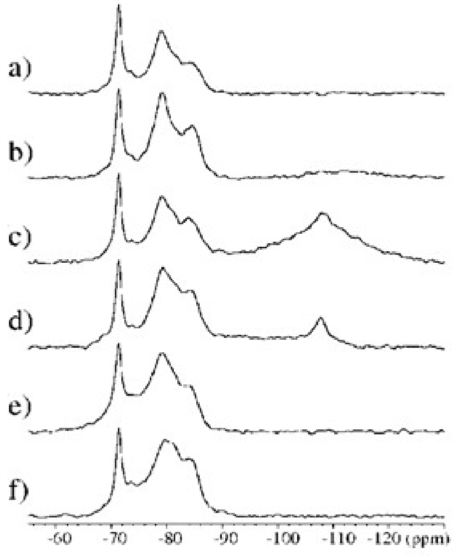

Figure 2: ^{29}Si MAS NMR spectra (9.4 T, ν_R = 12.0 kHz) of cement (WPC) – SCM pastes after 28 days of hydration. (a) Pure WPC, (b) 90 wt% WPC + 10 wt.% silca fume, (c) 70 wt% WPC + 30 wt% low-iron fly ash, (d) 70 wt% WPC + 30 wt% natural pozzolan, (e) 60 wt% WPC + 40 wt% slag S1, and (f) 60 wt% WPC + 40 wt% slag S2. From Poulsen et al. (2009).

5. 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.

New approaches combine a profile summation method with the Rietveld method using the PONKCS (Partial Or No Known Crystal Structure) approach (Scarlett and Madsen, 2006). 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. In case of SCMs this requires a separate scan of the SCM component for calibration of the technique. 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 can be obtained (Snellings et al., 2014). However, 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%.

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, making the appropriate choice and calibration of a fingerprint model for the C-S-H contribution essential in obtaining accurate quantification. For blends of Portland cement and fly ash, the PONKCS method has not been tried yet. However, the overlaps in the peak pattern of fly ash and C-S-H are relatively limited in some cases, and a relatively good accuracy may be expected.

In Figure 4, an example of the application of the PONKCS method to a hydrated 30% fly ash blended cement paste is shown. The phase constants of both the fly ash and C-S-H were determined from the unreacted SCM and a quartz blended mixture with 90 days of hydration (higher hydration degrees would be preferred to reduce the amount of alite in the reference sample to the minimum), respectively. This approach may not always be successful as the signals for fly ash and C-S-H overlap and the fitting of the model may be extremely sensitive to small inaccuracies in the determination of the phase constants. Also, a constant reaction degree is assumed over all phases from the fly ash. Moreover, it is quite possible that the 'phase constants' and the parameters diffraction signals for unblended and blended cement pastes are different due to C-A-S-H formation that the fly ash may cause depending on its composition.

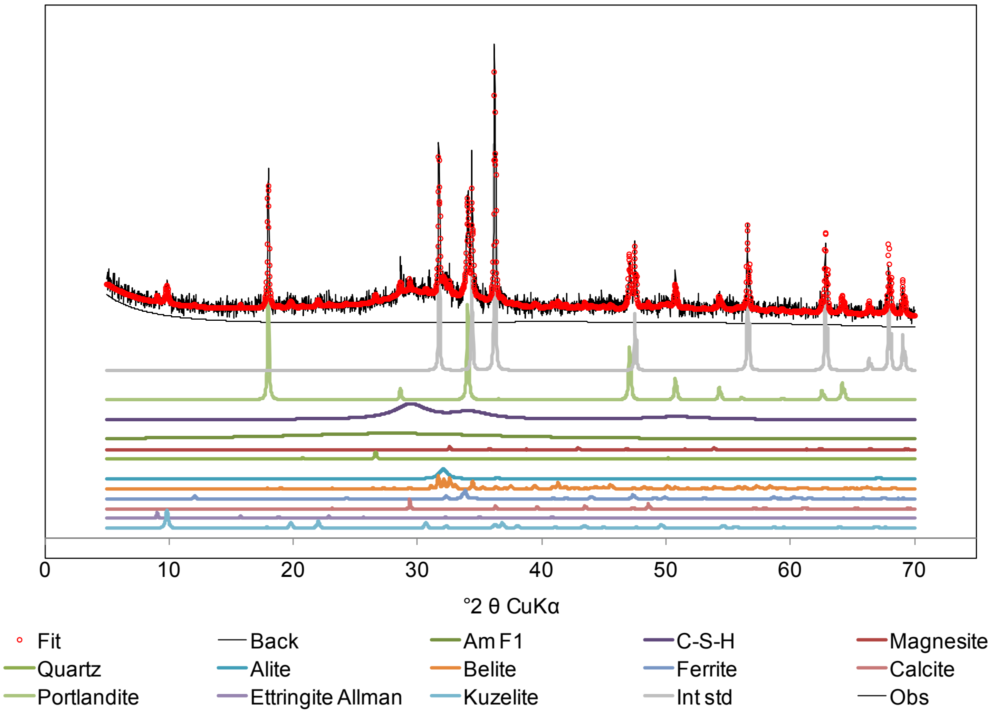

Figure 4: XRD patterns of fly ash blended cement paste (90 days of hydration), and decomposition in amorphous and crystalline phases. (Back: background; AmF1: amorphous fly ash; Obs: observed pattern).

The advantages of the PONKCS method are the 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 one hour. Furthermore, the method can be implemented easily into existing software packages for Rietveld analysis.

6. Indirect methods

Indirect methods rely on measuring the quantity of hydrates formed and then calculating the amount of 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. 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. (3) There is a significant change in the composition of the C-S-H phase between pure Portland cements and blended pastes. 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.

6.1. Thermogravimetic Methods

Many studies try to assess the degree of reaction of SCM from simple measurements of either bound water or calcium hydroxide. If acceleration of hydration of clinker phases and change in composition of C-S-H are taken into account, this is probably one of the least bad methods.

6.1.1. 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 1000°C. The average values of bound water per gram of reacted material are similar for different Portland cements and amount to 0.23-0.25 g/g ignited sample (Copeland and Kantro, 1960; Pane and Hansen, 2005). However, when SCMs are used it is complicated to separate the bound water due to reaction of the SCM from that due to the reaction of the clinker. Nonetheless, results of Portland and blended cements can be compared as an indication of differences in hydration process between the two types of binder.

The mass loss assumed to come from the chemically bound water (w_b) of the CH, C-S-H and other hydrates should be corrected for the mass loss due to decarbonation (around 650°C). An example of a TG and DTG analysis for a fly ash cement paste after 90 days of hydration is shown in Figure 5. Here, peaks for mass loss due to dehydration of ettringite (E), monosulphate (AFm) and portlandite (CH) are identified.

Pane and Hansen (2005) proposed a method based on the proportion of bound water at time t relative to the bound water at infinite time. Based on these principles, Gruyaert (2011) calculated the overall degree of reaction of Portland pastes and pastes with slag-to-binder ratios of 0.5 and 0.85. While the ultimate bound water content for pastes with a slag-to-binder ratio of 50% was similar as the bound water in Portland paste, a sharp decline was recorded for pastes with a slag-to-binder ratio of 0.85. 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. Furthermore, the degree of reaction calculated does not distinguish between the reaction of the SCM and clinker component.

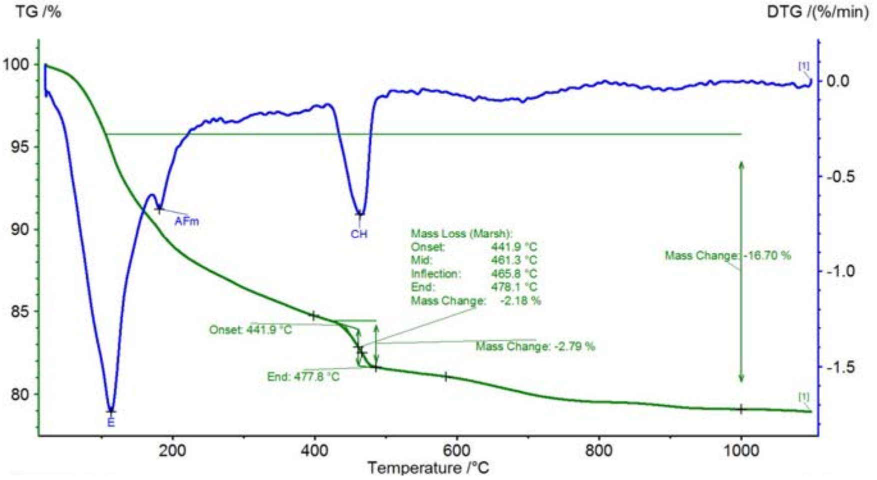

Figure 5: TG and DTG analysis of 30% fly ash cement paste after 90 days of hydration. E: ettringite; AFm: monosulphate; CH: portlandite.

6.1.2. Portlandite consumption

Alternatively, the pozzolanic reactions of fly ash or silica fume can be followed via the decrease of the amount of portlandite in the mixture (e.g. Cheng-yi and Feldman, 1985; Pane and Hansen, 2005). This method is well suited to assess on a comparative basis the increasing reaction of the SCM with time. Nevertheless, as the degree of reaction of the SCM is calculated from a relatively small measured difference in the portlandite content, a measurement error of ±2g/100g can lead to a relative error of ±50% in the degree of SCM reaction obtained. The experimental determination of portlandite by TGA or XRD often also deviate systematically as recently shown by De Schepper et al. (2014). In Figure 6, a comparison between the amount of portlandite in blended cement pastes determined by TGA and XRD/Rietveld analysis is shown. Here, the correlation is a little higher than the one shown in (De Schepper et al. 2014), but still in favor of a lower amount from the TGA method with tangential computation.

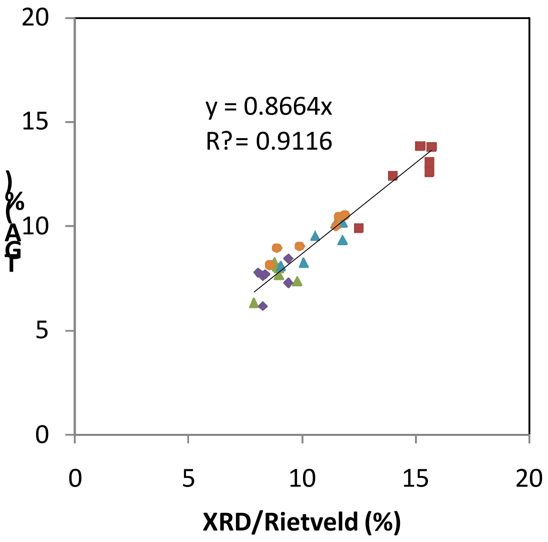

Figure 6: Portlandite contents in blended cement pastes determined by thermogravimetric analysis (TGA) and XRD/Rietveld analysis

Also, 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. Changes in C-S-H composition are another major source of error. Also, the formation of other phases, e.g. hemicarbonate or strätlingite, can strongly affect the portlandite consumption.

Figure 7 illustrates how the increase in hydration degree obtained from the bound water in fly ash cement pastes does not correspond with the evolution of the portlandite content. Here, data from 30% fly ash cement pastes with hydration degrees corresponding to 1; 7; 28 and 90 days of curing are presented. There is an initial increase in the portlandite content and bound water during the first days up to 7 days, but for 28 days the ratio CH/bound water decreases and for 90 days it is even lower than the initial ratio. From these differences, the reaction degree of the fly ash can be derived.

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 (1):

$$A_xS_y + (3x + yz)CH + x\,C\bar{X}_m + (xa + yb)H \rightarrow yC_zSH_b + xC_3ACX_mH_a \qquad (1)$$

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 equation 4 for the sake of clarity but may also be taken into account. 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. Lothenbach et al., 2011; Antoni et al., 2012; Deschner et al., 2012). 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.

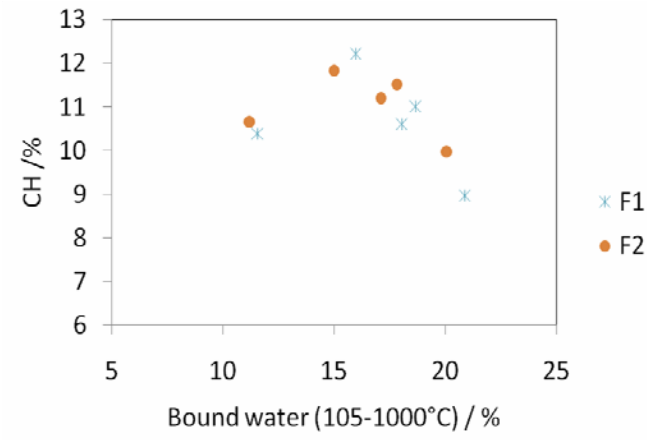

Figure 7: Evolution of portlandite content in function of the bound water content in two 30% fly ash cement pastes with increasing hydration degrees from 1 to 90 days.

6.1.3. 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. Gruyaert (2011) compared the calorimetric curves of blends containing slag with those of plain Portland cement mixes, normalised by the Portland cement content. They suggested the use of a fitting factor to bring the early reaction parts into alignment to account for the filler effect. 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.

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 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 (Costoya 2008). The method based on Geiker (1983) 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 into the pipette. The assemblage is then placed in a thermostatic bath. As the paste hydrates and the overall volume decreases, water is drawn into the paste and the level in the pipette descends. Some coloured oil placed on top of the water in the pipette allows to easily follow the drop in water level. As with 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. The exact stoichiometry and specific volumes of the hydrates formed, particularly C-S-H, are not well known. Specifically to assess the reaction degree of blends with fly ash, there is a lack of data to assess the usefulness of long term chemical shrinkage measurements and more work is needed here.

7. Conclusions

Measuring the degree of reaction of SCMs remains challenging. The traditional selective dissolution methods do not fulfil the prerequisites that the anhydrous Portland cement and the hydrates are completely dissolved, while the unreacted SCM should not dissolve at all. It should be checked on pure phases separately for re-precipitation. The picric acid method and the EDTA NaOH extraction would provide the best results, but the use of picric acid is not recommended due to its hazardous nature. The method can work better in “pure” systems, e.g. alkali activated or supersulfated slags when no clinker is present. The estimated accuracy is around ±10% at best.

Alternative methods have been developed, but 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. With regard to fly ashes, image analysis is very difficult. Due to the heterogeneous composition of fly ash, it contains phases with many and varied grey levels, which overlap with hydrates or clinker phases. Furthermore, an error will arise since small particles (< 2 μm) are not detected due to the resolution limit. New methods with quantitative EDS mapping to segment fly ash particles from the hydrated matrix and to follow the reaction of glass groups of disparate composition separately look very promising, but time consuming. NMR seems to be reliable but limited to fly ash with low iron content.

The possibility to quantify the amorphous phase by XRD is 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. However, the different reaction rates of different glasses in compositionally heterogeneous fly ashes will need to be accounted for and may strongly reduce the accuracy of the profile decomposition method.

Whereas for SCMs which react relatively fast (e.g. slag, calcined clay) the methods based on calorimetry and chemical shrinkage seem promising on a comparative basis, the very low reaction degree of fly ashes before 28 days means that the calorimetry method is not practical. There is a lack of data to assess the usefulness of long term chemical shrinkage measurements.

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 test 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.

8. Acknowledgements

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9. References

Antoni, M., J. Rossen, F. Martirena and K. Scrivener (2012). “Cement substitution by a combination of metakaolin and limestone.” Cement and Concrete Research 42(12): 1579–1589. doi:10.1016/j.cemconres.2012.09.006.

ASTM C1608 (2007). “Standard Test Method for Chemical Shrinkage of Hydraulic Cement Paste.” ASTM International, West Conshohocken Pennsylvania USA.

Baert, G. (2009). “Physico-chemical interactions in Portland cement – (high volume) fly ash binders.” PhD study, Ghent University (ISBN: 978-90-8578-298-8).

Ben Haha, M., K. De Weerdt and B. Lothenbach (2010). "Quantification of the degree of reaction of fly ash." Cement and Concrete Research 40(11): 1620-1629.

Cheng-yi, H. and R. F. Feldman (1985). "Hydration reactions in Portland cement-silica fume blends." Cement and Concrete Research 15: 585-592.

Copeland, L. E. and D. L. Kantro (1960). “Chemistry of hydration of Portland cement.” Symp. Cem. Chemistry, Washington, Cement and Concrete Association.

Costoya (2008) “Effect of particle size on the hydration kinetics and microstructural development of tricalcium silicate. Thèse EPFL, n° 4102 (

De Schepper, M., Snellings, R., De Buysser, K., Van Driessche, I., De Belie, N. (2014). " The hydration of cement regenerated from Completely Recyclable Concrete", Construction and Building Materials 60: 33-41.

Deschner, F., F. Winnefeld, B. Lothenbach, S. Seufert, P. Schwesig, S. Dittrich, F. Goetz-Neunhoeffer and J. Neubauer (2012). "Hydration of a Portland cement with high replacement by siliceous fly ash. " Cement and Concrete Research 42: 1389-1400.

Deschner, F., B. Münch, F. Winnefeld and B. Lothenbach (2013). "Quantification of fly ash in hydrated, blended Portland cement pastes by back-scattered electron imaging." Journal of Microscopy 251(2): 188-204.

DIN (German Institute for Standardisation) Technical Report CEN/TR 196-4: Prüfverfahren für Zement - Teil 4: Quantitative Bestimmung der Bestandteile (Test methods for cement – part 4: Quantitative determination of constituents). November 2007.

Durdzinski, P., Dunant, C.F., Ben Haha, M. and K.L. Scrivener (2015). “Identification of different glasses in calcareous fly ash and quantification of their degree of reaction in Portland-fly ash composite cements.” Submitted to Cement and Concrete Research.

Geiker, M. (1983). Studies of Portland Cement Hydration: Measurements of Chemical Shrinkage and a Systematic Evaluation of Hydration Curves by Means of the Dispersion Model. PhD study, Technical University of Denmark, Copenhagen.

Gruskovnjak, A., B. Lothenbach, F. Winnefeld, B. Münch, S. C. Ko, M. Adler and U. Mäder (2011). "Quantification of hydration phases in super sulphated cements: Review and new approaches."

Advances in Cement Research 23(6): 265-275.

Gruyaert, E. (2011). Effect of blast-furnace slag as cement replacement on hydration, microstructure, strength and durability of concrete. PhD study, Ghent University (ISBN: 978-90-8578-412-8).

Lothenbach, B., K. Scrivener, and R.D. Hooton, Supplementary cementitious materials. Cement and Concrete Research, 2011. 41(3): p. 217-229

Luke, K. and F.P. Glasser (1987). "Selective dissolution of hydrated blast furnace slag cements." Cement and Concrete Research 17(2): 273–282.

Ohsawa, S., K. Asaga, S. Goto and M. Daimon (1985). "Quantitative determination of fly ash in the hydrated fly ash - $CaSO_4{\cdot}2H_2O$ - $Ca(OH)_2$ system." Cement and Concrete Research 15(2):357-366.

Pane, I. and W. Hansen (2005). "Investigation of blended cement hydration by isothermal calorimetry and thermal analysis." Cement and Concrete Research 35(6): 1155-1164.

Poulsen S.L. (2009) "Methodologies for measuring the degree of reaction in Portland cement blends with supplementary cementititous materials by ^{29}Si and ^{27}Al MAS NMR spectroscopy", PhD thesis, Aarhus University, October 2009.

Scarlett, N. V. Y. and I. C. Madsen (2006). "Quantification of phases with partial or no known crystal structures." Powder Diffraction 21(4): 278–284. doi:10.1154/1.2362855.

Scrivener, K.L., Lothenbach, B., De Belie, N., Gruyaert, E., Skibsted, J., Snellings, R., Vollpracht, A. TC 238-SCM: Hydration and microstructure of concrete with SCMs. State of the art on methods to determine degree of reaction of SCMs. Materials and Structures, online.

Scrivener, K.L., H.H. Patel, P.L. Pratt and L.J. Parrott (1987). "Analysis of Phases in Cement Paste using Backscattered Electron Images, Methanol Adsorption and Thermogravimetric Analysis in Microstructural Development during the Hydration of Cement." Proceedings of Material Research Society Symposium, 85: 67–76.

Scrivener, K.L., T. Füllmann, E. Gallucci, G. Walenta and E. Bermejo (2004). "Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods." Cement and Concrete Research 34(9): 1541–1547. doi:10.1016/j.cemconres.2004.04.014.

Skibsted, J., M.D. Andersen and H.J. Jakobsen (2007). "Applications of solid-state Nuclear Magnetic Resonance (NMR) in studies of Portland cement-based materials." Zement Kalk Gips 60(6): 70-83.

Snellings, R., A. Salze and K.L. Scrivener (2014). "Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements." Cement and Concrete Research 64: 89-98.

Taylor, H.F.W. (1997), Cement Chemistry 2nd edition, Thomas Telford.

Vollpracht, A. and W. Brameshuber (2010). "Investigations on Ten Years Old Hardened Cement Paste Samples". Bagneux: RILEM. In: Proceedings of the International RILEM Conference on Materials Science (MatSci), Vol. III: Additions Improving Properties of Concrete (AdIPoC), Aachen, Ed. Brameshuber, W. (ISBN 978-2-35158-110-0): 79-91