Cement and Concrete Research 40 (2010) 1620–1629

Contents lists available at ScienceDirect

Cement and Concrete Research

journal homepage: http://ees.elsevier.com/CEMCON/default.asp

Quantification of the degree of reaction of fly ash

M. Ben Haha [a,*], K. De Weerdt [b,*], B. Lothenbach [a]

[a] Empa, Swiss Federal Laboratory for Materials Testing and Research, Laboratory for Concrete and Construction Chemistry, 8600 Dübendorf, Switzerland
[b] SINTEF Building and Infrastructure, 7465 Trondheim, Norway

ARTICLE INFO

Article history:
Received 23 April 2010
Accepted 16 July 2010

Keywords:
Blended cements
Chemical dissolution
Scanning electron microscopy (SEM)
Image analysis (IA)
Degree of reaction

ABSTRACT

The quantification of the fly ash (FA) in FA blended cements is an important parameter to understand the effect of the fly ash on the hydration of OPC and on the microstructural development. The FA reaction in two different blended OPC-FA systems was studied using a selective dissolution technique based on EDTA/NaOH, diluted NaOH solution, the portlandite content and by backscattered electron image analysis.

The amount of FA determined by selective dissolution using EDTA/NaOH is found to be associated with a significant possible error as different assumptions lead to large differences in the estimate of FA reacted. In addition, at longer hydration times, the reaction of the FA is underestimated by this method due to the presence of non-dissolved hydrates and MgO rich particles. The dissolution of FA in diluted NaOH solution agreed during the first days well with the dissolution as observed by image analysis. At 28 days and longer, the formation of hydrates in the diluted solutions leads to an underestimation. Image analysis appears to give consistent results and to be most reliable technique studied.

1. Introduction

The development of new materials and technologies utilizing waste and bi-products of industrial processes is an important task for the cement industry in their quest to reduce CO_2 emissions. Fly ash (FA) is a commonly used pozzolanic material in concrete, and many researchers have investigated its effect on the microstructure of concrete. Commercial fly ash blended cements in Europe can contain up to 35% of fly ash (CEM II). Due to regulations on CO_2 emissions cement producers are interested in replacing even larger parts of the Portland cement with fly ash. This gives new incentives to study high volume fly ash cements.

When combined with ordinary Portland cement, SiO_2 and Al_2O_3 originating from the glass phase of the FA will partly dissolve due to the high pH of the pore solution and will react with $Ca(OH)_2$ to form hydration products similar to the ones formed by ordinary Portland cement [1]. The determination of the amount of reacted as a function of time in fly ash blended cements enables to link the progress of the reaction of the different components (OPC, fly ash) and the subsequent changes.

FA gives a very broad X-ray peak which makes a quantification of unhydrated fly ash by XRD in the presence of other amorphous phases rather imprecise. Methods reported in literature to determine the amount of fly ash reacted include (i) selective dissolution methods, (ii) consumption of portlandite, and (iii) determination of fly ash reactivity in highly diluted solution.

Selective dissolution methods are commonly used techniques and aim at dissolving the hydrates and the unhydrated clinkers without dissolving the unreacted fly ash. This allows a direct determination of the amount of unreacted fly ash in a hardened cement paste as the unreacted fly ash remains as residue and can be quantified. A number of different methods have been reported in literature, generally based on the use of either acids or complexing agents.

Among all the acids reported in literature, picric acid appears to be the most promising for selective dissolution of hydrates and clinkers [2,3]. The method has been originally tested for a fly ash–gypsum–$Ca(OH)_2$ systems [2] and for hydrated cement pastes containing fly ash [3]. In the meantime the method has been employed in several studies [4–7]. In other studies, salicylic acid has been used as a dissolving agent as it is known to dissolve the silicates phases in OPC [8]. The technique appeared to be suitable when applied to a C_3S–fly ash systems [9,10]. However, when used in cementitious composite systems, it dissolved hydrates and interstitial (aluminates and ferrites) unreacted OPC phases insufficiently [2,11]. NaOH and sugar are known to dissolve the interstitial phases in unreacted OPC [8]. NaOH and sugar have been therefore combined with salicylic acid to study the fly ash reaction in blended cements [12]. The fraction of glass in fly ash reacted did not increase and agreed with the results found in previous studies [9,10]. Salicylic acid has also been tested in combination with hydrochloric acid (HCl) [11,13]. However, HCl was found to be too aggressive and to dissolve parts of the fly ash [2]. Acid conditions can also result in silica gel precipitation [11].

A frequently used complexing agent for selective dissolution of blended cements is ethylene diamine tetra acetic acid (EDTA) combined

---

* Corresponding authors. Haha is to be contacted at Tel.: +41 44 823 49 47; fax: +41 44 823 40 35. De Weerdt, Tel.: +47 73 59 48 66; fax: +47 73 59 71 36.

E-mail addresses: mohsen.ben-haha@empa.ch (M.B. Haha), klaartje.de.weerdt@sintef.no (K. De Weerdt).

0008-8846/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2010.07.004

with triethanolamine (TEA). It was first tried on slag blended cements [11] and later tested in a slightly adapted version on fly ash blended cements [14]. The EDTA method was not able to dissolve hydrotalcite and siliceous hydrogarnet-like phases and might have led to precipitation of amorphous silica [14]. The application of the EDTA/TEA method on fly ash was not a success [14].

In this study, different selective dissolution methods are compared on a hydrated fly ash cement pastes as previously reported comparative studies had been performed on “ideal systems” such as gypsum–$Ca(OH)_2$ [2] or on slag blended cements [11].

The pozzolanic reaction of the fly ash consumes $Ca(OH)_2$ to produce C–S–H. Thus the consumption of $Ca(OH)_2$ has been used as a measure for the degree of reaction of the fly ash [14]. The $Ca(OH)_2$ content in the hydrated OPC cement paste without fly ash is compared to the $Ca(OH)_2$ content in a corresponding paste containing fly ash. These results are difficult to interpret as not only the pozzolanic reaction influences the $Ca(OH)_2$ content but the fly ash also promotes clinker hydration due to the filler effect. Portland cement blended with fly ash shows initially a higher degree of reaction resulting in the presence of more portlandite than cement without fly ash [12]. This complicates the evaluation as it is difficult to assess where the filler effect ends and the pozzolanic reaction starts. Furthermore, there is the possibility that the dissolved silicate from the fly ash reacts directly with already formed C–S–H gel [15–17] rather than to precipitate in reaction with portlandite. This reaction mechanism will lead to lower Ca/Si ratio of the C–S–H instead of a decrease of the portlandite content.

A more theoretical approach to study the reactivity of fly ash is to investigate strongly diluted suspension of fly ash at high pH values [15]. The solution has been analyzed for Si, Al and K as a function of time and the obtained values are compared with Si, Al and K content of the glass phase in the FA. The fly ash was found to dissolve congruently; the difference in pH appeared to be more important than the difference in fly ash chemistry [15].

Backscattered electrons (BSE) images coupled with image analysis are a further possibility to quantify the reaction of fly ash in blended cements. BSE coupled with images analysis has been successfully used to quantify the reaction of Portland cement clinkers [18–20] and of blast furnace slags [21] and to study the extent of alkali aggregate reaction in concrete samples [22]. In this study the SEM-BSE images were analyzed quantitatively to get volume fractions of hydrated and unhydrated phases in the blended cement pastes. The segmentation of the unreacted fly ash particles was obtained using a combination of image analysis techniques such as grey-level threshold, and specific morphological filtering.

In this study different techniques of quantification of FA reaction in FA blended cements are evaluated and compared critically.

2. Materials and methods

2.1. Materials

The chemical composition of the Portland cement clinker, type F siliceous fly ash (FA) and limestone powder used in this study are given in Table 1. The $CaCO_3$ content of limestone determined by TGA is about 81%. The clinker has been interground with 3.7% of natural gypsum to obtain a total SO_3 content of 3% in the Portland cement. The used gypsum contained 0.2% free water, and had a $CaSO_4{\cdot}2H_2O$ content of 91.4%. The XRD-Rietveld of the FA indicates the presence of 18 wt.% mullite, 12 wt.% quartz and an amorphous content of 68 wt.% (Table 2). The amorphous content includes besides the glass phase, 3% of amorphous carbon. The composition of the glass phase given in Table 3 was calculated by subtracting the oxides present in the crystalline phases of FA (determined by XRD-Rietveld) from the total amount of oxides present in the FA as determined by XRF.

Table 1
Chemical composition of the clinker, fly ash and limestone in wt.%.

	Clinker	Fly ash	Limestone
SiO_2	20.8	50.0	12.9
Al_2O_3	5.6	23.9	2.7
Fe_2O_3	3.2	6.0	2.0
CaO	63.0	6.3	42.3
MgO	3.0	2.1	1.8
SO_3	1.5	0.4	–
P_2O_5	0.1	1.1	–
K_2O	1.3	1.4	0.6
Na_2O	0.5	0.6	0.5
Na_2O Eq.	1.4	1.6	
LOI	0.3	3.6	37.7
Carbon	–	3.1	–
Chloride	0.051	–	–
Free CaO	1.85	–	–
Blaine surface [m^2/kg]	310	450	900
Density [kg/m^3]	3150	2740	2490

2.2. Assessment of the degree of reaction

2.2.1. Selective dissolution

In this study, six different selective dissolution methods based on salicylic acid, hydrochloric acid (HCl), EDTA or picric acid have been tested and compared (see Table 4). The materials subjected to the selective dissolution experiments are:

- unhydrated OPC
- unreacted FA
- reacted OPC-FA = hydrated paste (80% OPC + 20% FA with w/b = 0.5 hydrated for 90 days at 20 °C)
- 80% reacted OPC-FA + 20% unreacted FA

The selective dissolution methods aim to dissolve selectively the hydrates and the unhydrated clinkers without dissolving the unreacted fly ash. The residue after dissolution is compared with the original sample mass to calculate the degree of reaction of the FA. The effectiveness of the different selective dissolution techniques were tested on the raw materials, unreacted FA and unhydrated OPC in order to identify techniques that dissolve all unhydrated clinker and hydrates without affecting the unreacted FA.

To study the efficiency of different dissolution techniques, on the “reacted OPC-FA”, consisting of the hydrated 80% OPC + 20% FA cured for 90 days at 20 °C: the residues after dissolution were examined using SEM techniques. To check for systematic errors, a fourth combination was tested, consisting of 80% reacted OPC-FA to which 20% unreacted FA was added. The weight difference of the residues between reacted OPC-FA and 80% reacted OPC-FA + 20% unreacted FA should be the weight corresponding to 20% FA considering the amount of residue not dissolved by the different dissolution techniques.

The unreacted FA and OPC were used as received for the selective dissolution. The hydrated pastes were treated prior to the selective dissolution with isopropanol and ether to stop hydration, ground to pass a 63 μm sieve and stored in a dessicator over silica gel. The powder was added to the solvent and stirred for the required time (Table 4). After mixing, the suspension was filtrated through a dried

Table 2
XRD-Rietveld analyses of the FA (wt.%).

	[g/100 g]
Quartz	12.3
Calcite	0.4
Hematite	0.6
Anhydrite	0.4
Mullite	18.3
Amorphous*	68.0

* glass and 3% amorphous carbon.

Table 3
Glass composition FA.

Glass*	[g/100 g]
SiO_2	54.1
Al_2O_3	17.9
Fe_2O_3	9.1
CaO	9.8
MgO	3.5
K_2O	2.4
Na_2O	1.0

*Glass composition calculated from XRF and Rietveld-XRD data.

and weighted Whatman GF/C filter (minimum particle size retained 1.2 µm). The residue was washed with distilled water, ethanol or methanol (see Table 4). The filter and residue were dried at 40 °C until a constant weight was reached. The weight of the samples was corrected for the water uptake during hydration using the dry weight as determined by TGA at 600 ° C.

2.2.2. Diluted alkaline solutions

The reaction of FA can be followed by measuring the dissolution of FA in a diluted alkaline solution [15] that has the same pH as observed in the pore solution of the cement paste (pH 13.6 for 65% OPC/+35% FA). The measured dissolved concentrations of Si and Al can be used to calculate the amount of dissolved glass of the FA.

0.050 g of FA was added to 50 ml 0.1, 0.2 and 0.5 mol/l NaOH solutions corresponding to a pH of 13.1, 13.3 and 13.7 respectively. After 1, 2, 3, 7, 14 and 28 days the Si content of the solution was analysed by a Dionex Ion Chromatography system (ICS) 3000 using Si standards from Fluka as reference. The Al content was only determined for the 0.5 mol/l NaOH solution using a simultaneous ICP-OES Varian Vista Pro.

To calculate the reaction of the FA, the dissolved quantities of Al and Si are compared to the glass composition as given in Table 3.

2.2.3. Scanning electron microscopy

An ESEM Philips FEG-XL30 microscope was used. The accelerating voltage of the beam was 15KV to provide a good compromise between spatial resolution and adequate excitation of the FeKα peak.

Table 4
Description of the different selective dissolution methods tested.

Methods	Chemicals needed/1 g sample	References
Salicylic acid	6 g salicylic acid 40 ml methanol *methanol**	[2,8–11]
Hydrochloric and salicylic acid	5 g salicylic acid 4.2 ml hydrochloric acid fill to 100 ml with methanol *methanol**	[13]
Hydrochloric acid	250 ml (1:20) hydrochloric acid *distilled water**	[30] [31]
EDTA/DEA	25 ml triethanolamine 9.3 g disodium EDTA*$2H_2O$ 17.3 ml diethylamine (DEA) fill to 100 ml with distilled water 1600 ml distilled water *distilled water**	[21,32]
EDTA/NaOH	500 ml disodium EDTA*$2H_2O$ (0.05 M) in NaOH (0.1 M) 500 ml distilled water 50 ml (1:1) triethanolamine:water 125 ml NaOH (1 M) to adjust pH *distilled water and ethanol**	[11,14,33]
Picric acid	11 g picric acid 60 ml methanol 40 ml distilled water methanol* 500 ml distilled water at 40 °C*	[2,3]

*Rinse solution.

2.2.3.1. *Residues of selective dissolution.* Polished sections of the residues of the different selective dissolution techniques were studied using both backscattered electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDS) to check the nature of the elements present in the residues.

2.2.3.2. *Reaction of the FA.* To study the reaction of FA, a slice was cut from the hydrated paste samples at different hydration times. The slices were immersed in isopropanol for 30 min to stop hydration and then dried in an oven for 1 day at 40 °C. After drying, the slices were vacuum impregnated with low viscosity resin and gradually polished down to 0.1 µm using diamond pastes. The drying and impregnation procedure did not induce any significant cracks. Backscattered electron (BSE) images of the polished sections were acquired using the ESEM. For the BSE imaging, the spot size was chosen to have a good resolution of the images. To avoid the charging effect, all specimens were coated with a thin film of carbon (around 5 nm). A typical BSE image and its corresponding grey level histogram are given in Fig. 1.

Image analysis of backscattered electron (BSE) images was carried applying different filters to the BSE images to get the volume fraction of unhydrated FA. The SEM-BSE images can be analysed to get volume fractions of phases in concrete, based on application of segmentation methods. The area fractions obtained from a 2D cross-section are equal to volume fractions from the 3D real structure when materials have a random and isotropic nature. The microstructure of cement paste can be considered to satisfy those stereological conditions [23].

As cementitious materials are heterogeneous, phase quantification by image analysis is usually done on a large number of fields in order to take into account the variations from one field to the other. Some

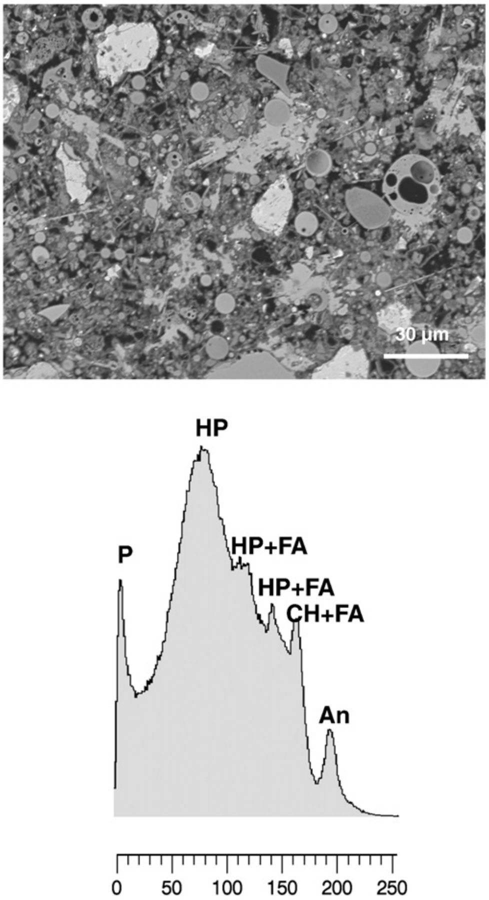

Fig. 1. Backscattered image of a FA blended cement at 28 days and its corresponding grey level histogram (P: porosity, HP: hydration products other than Portlandite, CH: Portlandite, An: unreacted clinker particle, FA: fly ash).

authors have tried to optimise the number of images to be taken, as a function of the magnification, to achieve the lowest standard error on the quantified phases [20,22,24]. At a magnification of 1600×, 60 images are found to be sufficient to include more than 20,000 FA particles which are large enough to ensure that the results are statistically relevant.

Concerning the BSE images of FA blended cements, there are many small FA particles. Omitting the small particles in the images could lead to great underestimation in volume fraction of unreacted FA in the pastes. Therefore, all images for the quantification are acquired with 1024 × 800 pixels at a magnification of 1600. The pixel size at this magnification is 0.14 µm. This is however not the minimum size measured as the threshold for any species involves an averaging effect whereby some pixels counted for the different species present in the images in fact contain some other species and vice versa corresponding to a threshold of approximately 1 µm. The result will remain always within the error of measurement of the technique. The magnification used offers the possibility to capture more than 97% of the starting material, as about 3% of the unreacted FA is smaller than 1 µm (see Fig. 2).

3. Assessment of the efficiency of selective dissolution methods

3.1. Mass differences

A comparison of the different selective dissolution methods is shown in the Table 5. The residue R is calculated by subtracting the weight of the filter, w_F, from the weight of the treated sample (TS) and the filter (F) after drying at 40 °C, w_{TS+F}. This value is reported relative to the dry weight of the hydrated sample (DS), obtained by TGA at 600 °C, $w_{DS} = w_{S,600\ ^{\circ}C}$:

$$R_S = \frac{w_{TS+F} - w_F}{w_{DS}}$$

An efficient technique should dissolve all unreacted OPC; the residue after selective dissolution should be close to zero. Comparing the residue of unreacted OPC in Table 5, it is clear that the method using salicylic acid is ineffective as 36% of the OPC remains undissolved after 3 h. If salicylic acid is used together with HCl or just HCl was used, more OPC is dissolved but if the samples are kept longer than 1 h in the solution, glassy particles have been observed to precipitate, most likely silica gel. The use of EDTA/DEA, EDTA/NaOH and picric acid resulted in a nearly complete reaction of the OPC (residue of about 2 wt.%).

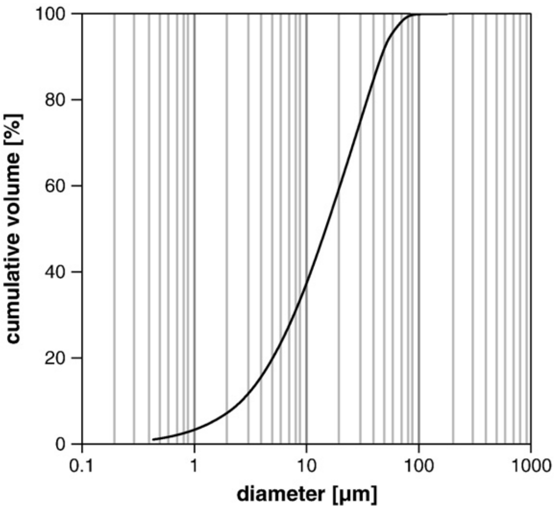

Fig. 2. Particle size distribution of FA obtained by laser granulometry.

Table 5
Assessment of the selective dissolution results: residue (R) as a % of the initial mass.

Method	Salicylic acid	Salicylic acid + HCl				HCl	EDTA/ DEA	EDTA/ NaOH	picric acid
Time	3 h	30 min	1 h	2 h	3 h	3 h	2 h	1 h	40 min
OPC	36.6	10.0	7.9	7.2	6.6	4.3	1.9	2.2	1.7
FA	96.9	93.4					90.7	92.2	82.5
reacted OPC-FA	47.2	22.2					15.8	17.2	12.2
% FA reacted	3.0	16.7					20.0	14.6	31.9
80%reacted OPC-FA + 20% FA	61.5	35.7					28.2	33.8	28.8
Expected	*57.1*	*36.4*					*30.7*	*32.2*	*26.2*

The ideal method should also leave the unreacted fly ash undissolved, resulting in a residue close to 100%. Comparing the results of the different applied selective dissolution techniques (Table 5), it can be seen that salicylic acid dissolves the least of the unreacted FA (3%) and picric acid the most (18%). The EDTA methods dissolve about 10% of the fly ash. The fact that the residue of the pure fly ash is not 100% could be explained by the dissolution of the finest and/or most reactive fly ash particles or the passing of the finest particles through the filter.

The percentage of fly ash reacted is calculated as follows:

$$\%FA = \left(\frac{R_{UP} - R_{HP}}{R_{UP}}\right) \times 100$$

$R_{UP} = R_{OPC} \times \%OPC + R_{FA} \times \%FA + R_L \times \%L$ with $\%OPC + \%FA + \%L = 100\%$ where R_{UP} is the calculated residue of the unhydrated blended paste which is the sum of the residues of the unreacted components (R_{OPC}, R_{FA} and R_L) and R_{HP} is the residue of the hydrated blended paste.

In the hydrated sample (reacted OPC-FA) a part of the FA should have reacted after 90 days. The residue should therefore be lower than the initial 20% FA content used. All methods, if the amount of unreacted OPC is considered, achieve this requirement. The calculated degree of FA reaction, however, varies from 3 to 32% with an error of measurement of ±1.0%, as the balance records with a sensitivity of 0.0001 g.

A good selective dissolution method is expected to be able to determine the amount of unreacted FA correctly. The residue of the hydrated sample (reacted OPC-FA) containing additional 20% of unhydrated FA should be close to the expected value, that is the sum of 80% of the residue of hydrated sample (reacted OPC-FA) and 20% of the residue of FA (the unreacted fly ash). Based on these results (see Table 5) all the methods perform about equally well.

3.2. Microscopic evaluation

The residues of the hydrated fly ash cement paste (reacted OPC-FA) were impregnated with epoxy resin and examined with SEM by backscattered (BSE) imaging coupled to energy-dispersive X-ray spectroscopy (EDS), see Fig. 3.

After extraction with salicylic acid, unreacted FA particles, hydration phases and certain parts of the unreacted OPC phases are still present (Fig. 3 A). The EDS point analyses show the presence of aluminium and sulphur rich phases as well as some silicate hydrates in the remaining hydration products. The presence of these hydration phases as well as unreacted OPC phases in the residue explains the high amount of residue found after the treatment (Table 5). In the unreacted clinker grains the silicate phases are dissolved and the iron and aluminum rich phases, C_3A and C_4AF, remain. These results are in agreement with the findings of Gutteridge [8] using the same method on unreacted cement. This method is thus not suitable for the determination of the degree of reaction of the fly ash.

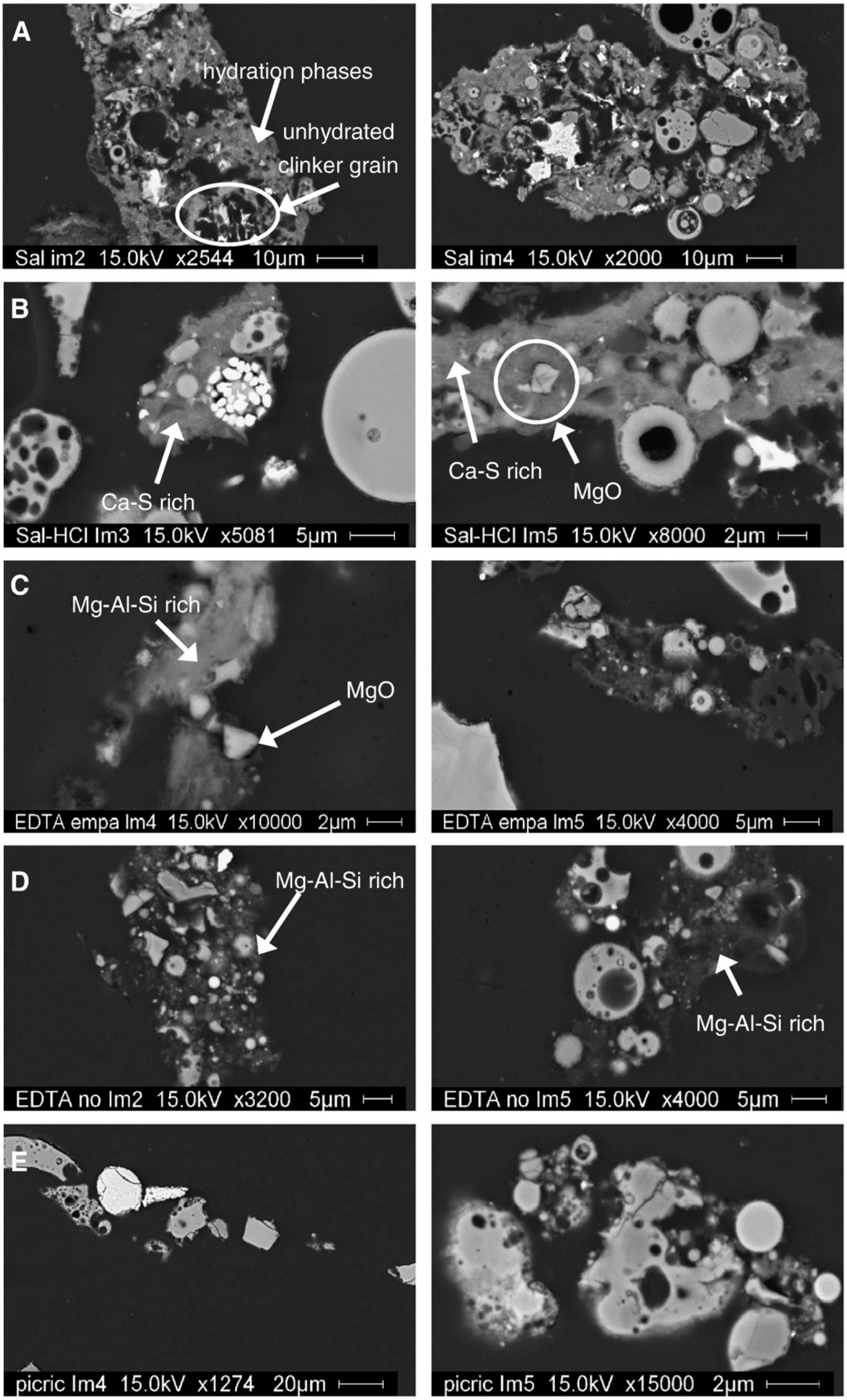

Fig. 3. Backscattered electron (BSE) image of the residues of OPC-FA reacted for 90 days after selective dissolution with A) salicylic, B) salicylic acid and hydrochloric acid, C) EDTA and DEA, D) EDTA and NaOH and E) picric acid.

The residues after the selective dissolution using both salicylic acid and hydrochloric acid contain besides unreacted fly ash particles and MgO particles, parts of the hydrated phases (Fig. 3 B). These parts are rich in calcium and sulfur with some traces of aluminium. This is in agreement with the previous reported results [13] that find that using this dissolution method only 1/3 of the gypsum dissolves. The presence of these Ca–S-phases might lead to a not neglectable residue due to the initial volume of the gypsum in the OPC.

After treating the hydrated paste with the EDTA and DEA (Fig. 3 C) a residue rich in Mg, Al and Si is found between the fly ash particles. The residue consists of unreacted fly ash particles and MgO particles and an amorphous phase rich in Mg, Al and Si.

The residue after treating the hydrated paste with the EDTA and NaOH method is found to be similar to the one found after treatment with EDTA and DEA (Fig. 3 D). Some pure MgO particles are embedded in this residue. The residue of a 65% OPC + 35% FA blended cement hydrated for 140 day examined by TGA exhibits a weight loss of 4% (50–600 °C), indicating the presence of hydration phases. The profile of the weight loss curve shows similarities to the weight loss pattern of hydrotalcite confirming the findings of the ESEM observation on the residue. Many clusters of fine fly ash particles are spotted when studying the residue. This might indicate that this method is not too aggressive towards finer fly ash particles.

Using picric acid, no hydration products are found in the residue (Fig. 3 E). Most remaining fly ash particles appear to be quite large. Only few clusters of finer particles can be observed when compared to the residues from the other techniques. This might indicate that treatment with picric acid dissolves a part of the smaller fly ash particles.

3.3. Comparison of the selective dissolution techniques

From both the evaluation of the mass of the different residues and the examination of the residues with SEM it can be concluded that salicylic acid is not suitable for the purpose of determining the degree of reaction of FA as it does not dissolve the hydration phases and certain unreacted OPC phases (C_3A and C_4AF). The performance of the selective dissolution improves when salicylic acid is combined with hydrochloric acid. No unhydrated clinker phases were found, but still an amorphous residue of hydration phases rich in Ca and S is detected. This introduces errors in the determination of the degree of reaction of the fly ash. Selective dissolution using picric acid results in the smallest residue for the hydrated paste. The residue consists only of not too small unreacted fly ash particles. No residues of hydration phases or unreacted clinker grains are found, but 18% of the unhydrated FA has dissolved. This method seems to be rather too harsh for determining the degree of reaction of the fly ash. In addition, picric acid can be explosive upon drying [25,26]. Thus this method is not recommended. The two EDTA selective dissolution techniques using DEA or NaOH lead to similar results. The residue after the selective dissolution consists of unreacted fly ash particles, Mg-rich particles and a Mg–Al–Si rich amorphous phases. The presence of these amorphous phases in the residue leads to an error in the determination of the degree of reaction of the fly ash in fly ash blended cements. By comparing the systematic error, the ability to determine the amount of unhydrated FA correctly (Table 5), user-friendliness and the residues, it can be concluded that the EDTA with NaOH appears to be the most suitable selective dissolution method to determine the degree of reaction of the fly ash in hydrated FA blended cement pastes.

4. Determination of FA reaction in blended systems

The degree of reaction of FA over time was determined in two different FA blended cement systems containing 65% OPC + 35% FA and 65% OPC + 30% FA + 5% L, respectively. Cement pastes with water to binder ratio of 0.5 were prepared using a vacuum mixer from Renfert. The paste was poured in to 60 ml cylindrical plastic bottles and stored under sealed conditions at 20 °C.

4.1. EDTA with NaOH

The results of the selective dissolution with EDTA and NaOH are given in the Table 6; 92% of the unreacted FA, 2% of the OPC and 17% of the limestone remain after treatment. The 2% residue of the OPC might be related to the MgO particles present in the OPC which do not dissolve by the EDTA and NaOH treatment, as shown by the ESEM and TGA investigation of the residues. The 17% residue of the limestone corresponds to the quantity of impurities present (Table 1). The 8% of FA which disappears during the EDTA treatment might either slip through the filter or is due to the dissolution of readily soluble small particles or phases present in the FA. To check the importance of the passing size, a finer filter (0.7 μm) was used. However, no differences in the residues are observed.

Table 6

Reaction of FA in cement pastes containing 65% OPC + 35% FA and 65% OPC + 30% FA + 5% L determined by dissolution in diluted alkaline solution (DA), image analysis (IA) and selective dissolution (with EDTA/NaOH).

		DA		*IA*	Selective dissolution		
	Time				% FA reacted		Residue*
	[day]	Si	Al		min	max	
100% FA							*92*
100% L							*17*
100% OPC							*2*
65% OPC	0	0	0	–	0	9	*33*
+ 35% FA	1	1	3	2	−2	7	*34*
	7	5	12	8	0	9	*33*
	28	10	22	21	3	12	*32*
	90	14	32	30	9	18	*30*
	140	–	–	35	11	19	*30*
65% OPC	0	0	0	–	0	8	*30*
+ 30% FA	1	1	3	1	−3	5	*31*
+ 5% L	7	5	12	6	0	8	*30*
	28	10	22	22	3	12	*29*
	90	14	32	29	9	17	*27*
	140	–	–	35	12	20	*26*

*Residues from the selective dissolution used for the calculations.

The residues are calculated as described in the Section 3.1. Those of the hydrated pastes are corrected for residues of the raw materials (FA, limestone and OPC). Concerning OPC and L, their residues have only a minor effect on the calculated % of reacted FA. However, the residue of FA has a significant impact (up to 8%). Omitting the later correction leads to an overestimation of the amount of FA reacted at early age, but it might be more accurate at later age as the part of the unreacted FA that dissolves in the selective dissolution (small reactive particles), might have reacted anyway during hydration.

Minimal and maximal values are reported in Table 6 and Fig. 4 as different assumptions can be made for the calculations. At early reaction times, it might be appropriate to use the measured residue of the unhydrated OPC and FA, to calculate the degree of reaction (minimal value). At later ages, however, all the small particles originally present in the FA might have reacted completely, so that this correction is no longer adequate but better the theoretical amount of FA (35% or 30% FA) is used (maximal value). The difference between the two assumptions is significant (up to 8% of difference in % reacted FA), see Table 6.

The reproducibility of the selective dissolution is high; a standard deviation of 0.2% on a 32.1% residue was obtained on triplicate samples, an error which is very small compared to the error introduced by the assumptions needed to calculate the amount of FA reacted. These assumptions are a major cause of errors, rendering this method inadequate for quantifying the degree of reaction of FA.

The percentage of FA reacted determined with the three different methods for the 65% OPC + 35% FA and 65% OPC + 30% FA + 5% L blends are compared in Fig. 4. The percentage of FA reacted determined by selective dissolution is generally lower than the values obtained by other methods. This underestimation is probably due to the presence of hydrates in the residue (in TGA a weight loss of the residue of up to 4 wt.% is observed).

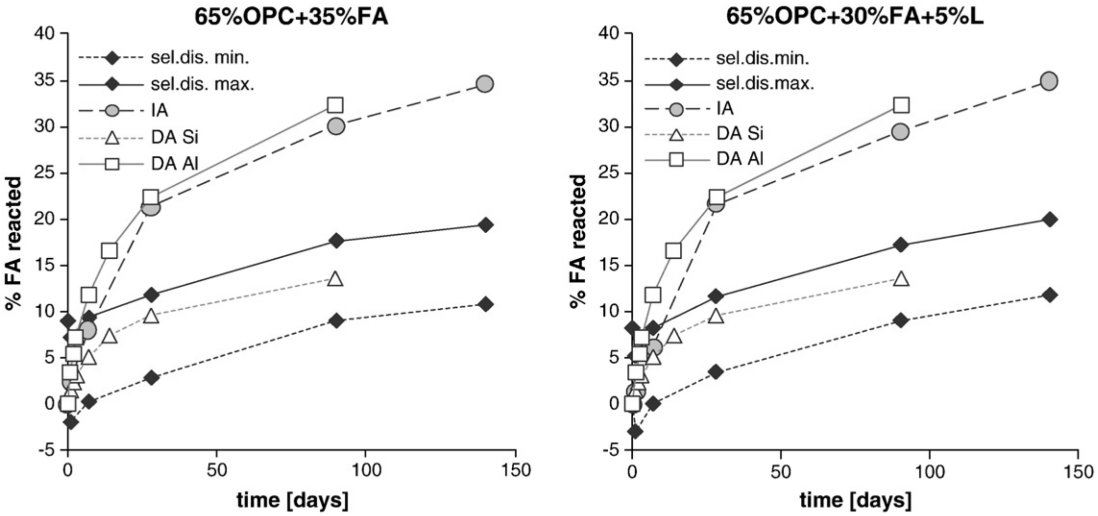

Fig. 4. The % of FA reacted in the two tested mixes determined by image analysis (IA), FA dissolution in 0.5 mol/l NaOH (DA) and selective dissolution using EDTA/NaOH (sel.dis. min./max.).

4.2. Diluted alkaline solutions

The dissolution of FA can be determined in alkaline solutions by measuring silicate or aluminium concentration as a function of time and comparing it with the SiO_2 or Al_2O_3 content in the glass of the FA [15].

$$\%FA\ reacted = \frac{[X_{meas}]}{[X_{tot}]} \times 100;$$

where X is the measured species (Al or Si), $[X_{meas}]$ is the measured concentration and $[X_{tot}]$ is the total concentration assuming a total dissolution of the amorphous part of the FA.

The FA dissolves faster at higher NaOH concentrations (Fig. 5). The pH in the FA cements during the first 90 days has been determined to be 13.6, close to the pH 13.7 of the 0.5 mol/l NaOH solution. The Al concentration in the solution is considerably higher than the Si concentration relative to their initial amount in the glass composition (Fig. 5) indicating an inhomogeneous glass dissolution, due probably to a preferential dissolution of Al from FA glass or to the precipitation of the Si in a gel. The FA still present after 28 days is conglomerated indicating the formation of reaction products.

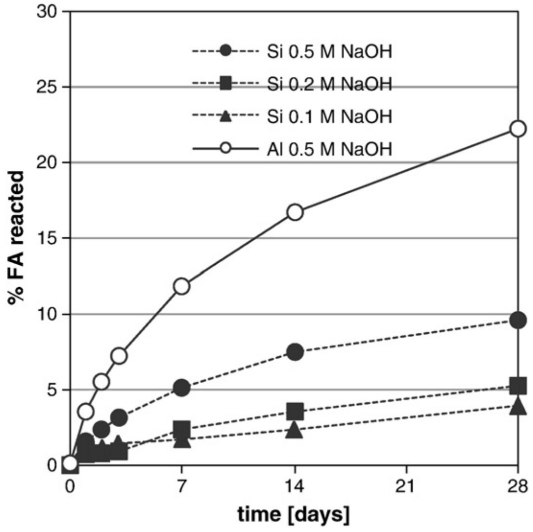

Fig. 5. % FA reacted calculated based on measured Al and Si concentrations resulting from FA dissolution in different NaOH solutions.

The amount of FA reacted based on the Al concentration in the 0.5 M NaOH solution is comparable to the results obtained by image analysis (IA) (see Fig. 4). The degree of reaction of FA calculated from the Si concentration results in a lower degree of dissolution from 7 days when compared to both IA and Al concentrations.

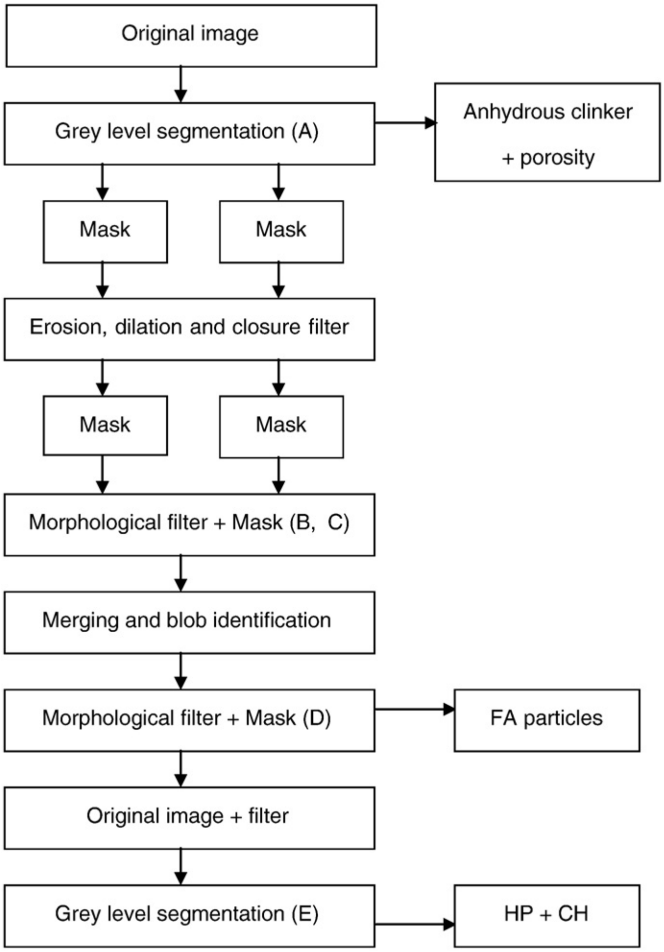

Fig. 6. Image processing sequence. Letters (A, B, C, D and E) refer to the steps shown in Fig. 7.

4.3. Image analysis

Backscattered electron imaging provides image contrast as a function of element composition [23]. The grey level of BSE image is directly proportional to the backscattered coefficient which is related to the atomic weight. Accordingly, the higher the average atomic number, the brighter it is in the backscattered image. Since the images are acquired in 8 bits, 256 grey level values are included in the image, ranging from 0, black (porosity) to 255, white. The BSE image and grey level histogram of FA blended cement hydrated for 28 days are given in the Fig. 1. Typical constituents of a hydrated OPC can be distinguished by their grey levels: unreacted OPC phases appear bright, calcium hydroxide (CH) light grey, other hydration products grey and porosity black [19]. However, for blended fly ash cements it turns more complicated as the FA particles have different grey levels depending on their chemical composition. Their grey level is within the range of C–S–H and CH. The challenge in this approach is therefore to correctly distinguish the FA from the cement matrix.

In this paper a new method is proposed for quantitative measurements of the reaction degree of FA in hardened cement paste using image analysis (IA) techniques applied on BSE images. The method developed for the segmentation of the unreacted FA particles is similar to the procedure reported in the literature [22,27] for the segmentation of aggregates from a concrete matrix. It is not possible to segment the FA purely on the basis of grey level due to the overlap. Therefore various morphological filters are applied in different steps of the segmentation as described in the Fig. 6.

Morphological operations apply a structuring element. A 3×3 element is used for this study. Setting the size of the structuring element is similar to setting the observation scale and setting the criterion to differentiate image objects or features according to size. In general, smaller structuring elements preserve finer details within an image than larger elements. The operation compares the element to the underlying image and generates an output pixel based upon the function of the morphological operation. The size and shape of the structuring element determines what is extracted or deleted from an

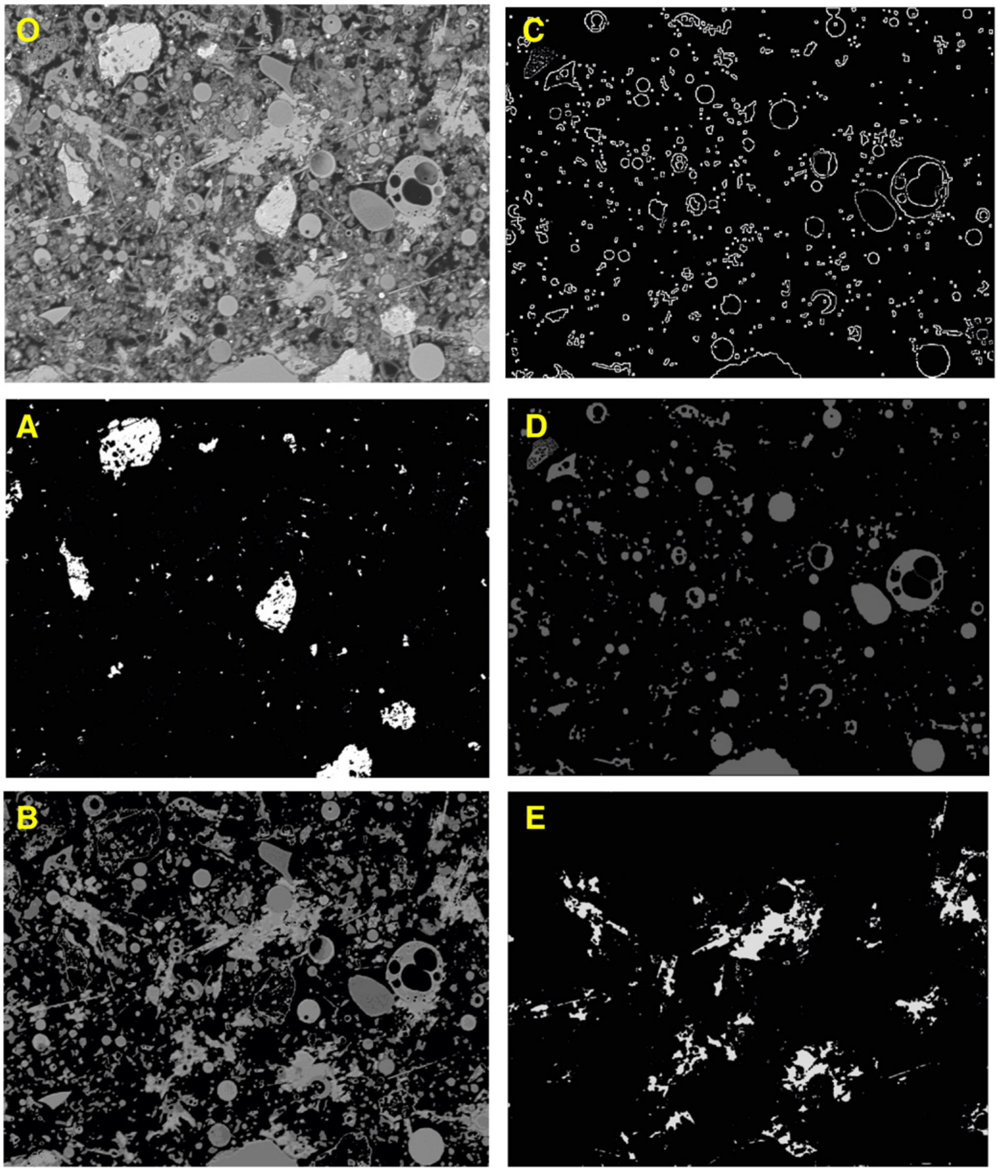

Fig. 7. Original BSE image (O) of Fig. 1 and different steps of segmentation leading to A (anhydrous clinker), D (anhydrous FA) and E (calcium hydroxide CH) obtained by the application of proposed image analysis procedure.

image. When applying morphological operations to a greyscale level, each pixel value is compared to the neighbourhood minimum or maximum value (as required by the morphological process).

The blob filter is used after segmentation to group pixels in some meaningful way into blobs of a single color with black pixels being the background [28,29]. When the image is grouped into blobs, the mask filters are used to remove the pixels remaining in the image that are not wanted.

In order to follow the reaction over time of FA particles, well polished thin sections of pastes at different ages of reaction are required. A good polishing is a key factor for a good image analysis. The application of the morphological filter to get out the FA particles could miss edges of the particles in not well polished surfaces presenting sharp edges. However, this error involves only the contours of FA particles these are estimated to 2.5% of the total volume of FA. This value will contribute to the systematic error of the method in not well polished samples.

The threshold of 1 μm could lead to an overestimation of the FA reaction. Nevertheless, this overestimation is controlled by comparing the original and segmented images. The results obtained at 1 day using SEM-IA (around 2% of FA reacted for both systems) show that these error are fairly low for the FA investigated.

The BSE-IA technique enables the quantification of the content of unreacted FA particles. Additionally, the total volumes of unreacted cement, CH, other hydrates or capillary porosity is obtained (see Fig. 7). However, in this paper we focus on quantifying the FA.

The degree of reaction of FA is obtained by subtracting the content of unreacted FA determined by IA from the initial FA content and dividing it by the initial FA content.

$$\%FA\ reacted = \left(1 - \frac{V_{meas}}{V_{ini}}\right) \times 100;$$

where V_{meas} is the volume of FA obtained from the IA and V_{ini} is the initial volume of FA in the mix proportions.

The data as shown in Table 6 and Fig. 4 indicate little reaction during the first day ($\leq 2\%$) confirming that at least 98% of the FA particles are visible by IA. The FA continues to react at a rather steady rate during the first 28 days (Fig. 4), at longer hydration times the reaction rate of FA slows down, resulting in a total reaction of the FA of 35% after 140 days.

The SEM image analysis is a direct method for the calculation of the degree of reaction. Indeed, from the segmented images the different phase assemblages could be controlled visually in order to verify whether the segmentation process is accurate or not. A combination of filters and grey level thresholding was applied to distinguish between the unreacted FA and the hydrated phases. The results at early age show no overestimation of the reaction degree of FA, indicating accurate quantification of these phases. The results of the IA during the first week are comparable to the reaction determined in diluted alkaline solutions (Fig. 4). However, at later ages the results of the diluted solution diverges between Al and Si and some precipitates are observed. In the diluted solution method, a nearly infinite medium is available around FA particles: 0.05 g of FA in 50 ml of the solvent, which does not represent the situation in concrete. Additionally, other ions that may interact with FA particles to enhance or retard its dissolution are missed. The use of SEM-IA for quantifying the reactivity of the FA particles in the FA blended cements is a relatively simple and reliable method even if it requires advanced equipment and it is time consuming.

5. Conclusions

Different methods to determine the degree of reaction of FA in blended cement were evaluated and compared: selective dissolution, dissolution of FA in a diluted alkaline solution and image analysis. The techniques use different approaches: selective dissolution uses the weight fraction of phases; the dissolution rate is based on the concentration values in the solution, while the SEM image analysis is calculated from the volume change of unreacted FA.

Selective dissolution, 0.5 NaOH diluted solution and IA indicate that in both the OPC–FA and the OPC–FA–L mixture all the FA reacts significantly during the first 28 days and the reaction slows down later.

During the first 90 days, the degree of reaction of the FA measured by SEM-IA agrees well with the degree of reaction determined by Al-dissolution in alkaline solution even if the conditions are different (cementitious environment and alkaline solution). The Si concentration underestimate the FA reaction. After 28 days, conglomerates were observed in the alkaline solution, which lead to an underestimation of the degree of reaction of FA using the dilution method.

The difference in the degree of reaction between the maximum values of selective dissolution and SEM-IA starts to be very significant after 28 days, due to the presence of hydrates in the residues of the selective dissolution (Fig. 3D) leading to an underestimation of the FA reaction for the selective dissolution method. The different assumptions and corrections as well as to the presence of hydration products in the residues as observed by SEM and TGA introduce a large error in the degree of reaction determined by selective dissolution.

The SEM image analysis technique gave the most reliable and consistent results of the degree of reaction of FA in FA blended cements.

Acknowledgements

The authors would like to acknowledge COIN, the COncrete INnovation centre (http://www.coinweb.no) for facilitating the cooperation and the financial support; Frank Winnefeld and Florian Deschner for their helpful discussions of the experimental setup and the results; Harald Justnes for his helpful comments; Zajac Maciej for his contribution concerning the dissolution techniques; Gwenn Le Saout for the Rietveld analysis of FA; Boris Ingold for the excellent preparation of the polished SEM samples and Luigi Brunetti for his help on the selective dissolution experiments.

References

[1] H.F.W. Taylor, Cement chemistry, Thomas Telford publishing, London, 1997.

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

[3] S. Li, D.M. Roy, A. Kumar, Quantitative determination of pozzolanas in hydrated systems of cement or Ca(OH)2 with fly ash or silica fume, Cement and Concrete Research 15 (1985) 1079–1086.

[4] S.K. Antiohos, A. Papageorgiou, V.G. Papadakis, S. Tsimas, Influence of quicklime addition on the mechanical properties and hydration degree of blended cements containing different fly ashes, Construction and Building Materials 22 (2008) 1191–1200.

[5] G. Baert, Physico-chemical interactions in Portland cement — (high volume) fly ash binders, PhD, Faculty of Engineering, Ghent University, , 2009.

[6] L. Lam, Y.L. Wong, C.S. Poon, Degree of hydration and gel/space ratio of high-volume fly ash/cement systems, Cement and Concrete Research 30 (2000) 747–756.

[7] Y.M. Zhang, W. Sun, H.D. Yan, Hydration of high-volume fly ash cement pastes, Cement and Concrete Composites 22 (2000) 445–452.

[8] W.A. Gutteridge, On the dissolution of the interstitial phases in Portland cement, Cement and Concrete Research 9 (1979) 319–324.

[9] K. Mohan, H.F.W. Taylor, Pastes of tricalcium silicate with fly ash — analytical, electron microscopy, trimethylsilylation and other studies, Material Research Society, Annual Meeting (1981) 54–59.

[10] K. Ogawa, H. Uchikawa, K. Takemoto, I. Yasui, The mechanism of the hydration in the system C3S-pozzolana, Cement and Concrete Research 10 (1980) 683–696.

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

[12] J.A. Dalziel, W.A. Gutteridge, The influence of pulverized fuel ash upon the hydration characteristics and certain physical properties of a Portland cement paste, Cement and Concrete Association, technical report 560, 1986, 28 pages.

[13] B.A. Suprenant, G. Papadopoulos, Selective dissolution of Portland Fly Ash cements, Journal of Materials and Civil Engineering 3 (1991).

[14] K. Luke, F.P. Glasser, Internal chemical evolution of the constitution of blended cements, Cement and Concrete Research 18 (1988) 495–502.

[15] H.S. Pietersen, The reactivity of fly ash in cement, PhD thesis, TU Delft, (1993).

[16] P.L. Rayment, The effect of pulverised-fuel ash on the c/s molar ratio and alkali content of calcium silicate hydrates in cement, Cement and Concrete Research 12 (1982) 133–140.
[17] H.F.W. Taylor, K. Mohan, G.K. Moir, Analytical study of pure and extended Portland cement pastes: II, fly ash- and slag-cement pastes, Journal of the American Ceramic Society 68 (1985) 685–690.
[18] M. Mouret, A. Bascoul, G. Escadeillas, Study of the degree of hydration of concrete by means of image analysis and chemically bound water, Advanced Cement Based Materials 6 (1997) 109–115.
[19] K.L. Scrivener, Backscattered electron imaging of cementitious microstructures: understanding and quantification, Cement and Concrete Composites 26 (2004) 935–945.
[20] K.L. Scrivener, H.H. Patel, P.L. Pratt, L.J. Parrott, Analysis of phases in cement paste using backscattered electron images, methanol adsorption and thermogravimetric analysis, Proceeding Material Research Society Symposium, Microstructural Development During the Hydration of Cement (1986) 67–76.
[21] A. Gruskovnjak, B. Lothenbach, F. Winnefeld, B. Münch, R. Rigi, S. Ko, M. Adler, U. Mäder, Quantification of hydration phases in supersulphated cements : review and new approaches, Advances in cement research, (Submitted).
[22] M. Ben Haha, E. Gallucci, A. Guidoum, K.L. Scrivener, Relation of expansion due to alkali silica reaction to the degree of reaction measured by SEM image analysis, Cement and Concrete Research 37 (2007) 1206–1214.
[23] K.L. Scrivener, T. Füllmann, E. Gallucci, G. Walenta, E. Bermejo, Quantitative study of Portland cement hydration by X-ray diffraction/Rietveld analysis and independent methods, Cement and Concrete Research 34 (2004) 1541–1547.
[24] M. Mouret, E. Ringot, A. Bascoul, Image analysis: a tool for the characterisation of hydration of cement in concrete — metrological aspects of magnification on measurement, Cement and Concrete Composites 23 (2001) 201–206.
[25] P.C. Ashbrook, T.A. Houts, Picric acid, Chemical Health and Safety 10 (2003) 27–???.
[26] G. Lunn, E.B. Sansone, Destruction of hazardous chemicals in the laboratory, John Wiley & Sons, New York, 1990, pp. 219–221.
[27] R. Yang, N.R. Buenfeld, Binary segmentation of aggregate in SEM image analysis of concrete, Cement and Concrete Research 31 (2001) 437–441.
[28] T. Jiang, M.B. Merickel, Identification and boundary extraction of blobs in complex imagery, Computerized Medical Imaging and Graphics 13 (1989) 369–382.
[29] D. Marr, E. Hildreth, Theory of edge detection, Proceedings of the Royal Society of London Series B, Biological Sciences 207 (1980) 187–217.
[30] A. Fernández-Jiménez, A.G. de la Torre, A. Palomo, G. López-Olmo, M.M. Alonso, M.A.G. Aranda, Quantitative determination of phases in the alkaline activation of fly ash. Part II: degree of reaction, Fuel 85 (2006) 1960–1969.
[31] K. Dombrowski, A. Buchwald, M. Weil, The influence of calcium content on the structure and thermal performance of fly ash based geopolymers, Journal of Materials Science 42 (2007) 3033–3043.
[32] J.S. Lumley, R.S. Gollop, G.K. Moir, H.F.W. Taylor, Degrees of reaction of the slag in some blends with Portland cements, Cement and Concrete Research 26 (1996) 139–151.
[33] H.M. Dyson, I.G. Richardson, A.R. Brough, A combined [29]Si MAS NMR and selective dissolution technique for the quantitative evaluation of hydrated blast furnace slag cement blends, Blackwell, Malden, MA, ETATS-UNIS, 2007.