

# Recommendation of RILEM TC 238-SCM: determination of the degree of reaction of siliceous fly ash and slag in hydrated cement paste by the selective dissolution method

Yury A. Villagrán-Zaccardi · Anya Vollpracht · Elke Gruyaert · Nele De Belie

Received: 6 September 2017 / Accepted: 29 December 2017  
© RILEM 2018

**Abstract** The performance of slag and fly ash in hydrated cementitious materials depends on the degree of reaction developed at the evaluated age. Several methods for the determination of the reaction degree of supplementary cementitious materials are available, among which the selective dissolution method is one of

methods developed the earliest. This is a direct method that aims to quantify the amount of unreacted slag or fly ash in the sample by applying a selective acid attack. The degree of reaction is obtained from the comparison between the remaining unreacted SCM, which should not dissolve, and the total amount initially included in the mix. This recommendation indicates suitable procedures for computing the degree of reaction by selective dissolution of cement pastes containing slag and fly ash. Specific considerations are indicated for necessary corrections due to the imperfect selective dissolution when the procedure is applied to hydrated cement paste.

---

This recommendation has been prepared by a number of members of work group 2 within RILEM TC 238-SCM. The recommendation has been reviewed and approved by all members of the TC 238-SCM.

---

*TC Membership:*

*Chair:* Nele De Belie.

*Secretary:* Barbara Lothenbach.

*TC Members:* Natalia Alderete, Eleni Arvaniti, Susan A. Bernal, Wolfgang Brameshuber, Anja Buchwald, Laurie Buffo-Lacarriere, Carmen Andrade, Jacek Chwast, Luc Courard, Nele De Belie, Christos Dedeloudis, Emmanuel Denarié, Yuvaraj Dhandapani, Josée Duchesne, Pawel Durdzinski, Jan Elsen, Mette Geiker, Fred Glasser, Elke Gruyaert, Duncan Herfort, R. Doug Hooton, Maria G. Juenger, Hao Huang, Harald Justnes, Agnieszka J Klemm, Konstantin Kovler, Barbara Lothenbach, Thomas Matschei, Winnie Matthes, Esperanza Menéndez Méndez, Toyoharu Nawa, Angela Nunes, Cedric Patapy, John Provis, Jay G. Sanjayan, Manu Santhanam, Siham Kamali-Bernard, Marina Kozhukhova, Karen Scrivener, Kosmas Sideris, Ruben Snellings, Konstantin Sobolev, José F. Martirena-Hernández, Tongbo Sui, Marios Soutsos, Nguyen Van Tuan, Yury A. Villagrán-Zaccardi, Jeanette Visser, Anya Vollpracht, Fengzhe Wang, Guang Ye, Jian Zhou, Semion Zhutovsky, Monika Zervaki.

**Keywords** Degree of reaction · Selective dissolution · Acid attack · Slag · Fly ash · Supplementary cementitious materials

---

Y. A. Villagrán-Zaccardi · E. Gruyaert · N. De Belie  
Magnet Laboratory for Concrete Research, Ghent University, Tech Lane Ghent Science Park, Campus A, Zwijnaarde-Technologiepark 904, 9052 Ghent, Belgium

A. Vollpracht  
Institute of Building Materials Research, RWTH Aachen University, Schinkelstr. 3, 52062 Aachen, Germany

Y. A. Villagrán-Zaccardi (✉)  
LEMIT, CONICET, 52 entre 121 y 122 s/n,  
1900 La Plata, Argentina  
e-mail: yuryvillagran@conicet.gov.ar

## 1 Introduction/scope

The extent of the reaction of supplementary cementitious materials (SCM) in hydrated cement paste is a key issue for connecting its effects with the pore structure of the cementitious material.

Different methods can be used for this purpose, and they can be classified as direct and indirect methods [1]. The direct methods aim to quantify the amount of unreacted SCM in the mix. The indirect methods are based on the quantification of some phases in the hardened material, which are affected by the reaction of SCM. Selective dissolution is thus classified as a direct method.

The purpose of the selective dissolution method is to dissolve all phases that are present in the hardened material, except unreacted SCM. This is never completely achieved, as part of the unreacted SCM can be dissolved and some small amounts of the other phases remain undissolved. An acceptable result is to be expected when these relative amounts are below 10% of the total content of the respective phases. In fact, based on the appropriate definition of the method, it should be better called 'preferential dissolution'.

The accuracy and repeatability of the method have been contrasted with other methods, such as backscattered electron image analysis, portlandite consumption assessed by thermogravimetry, and XRD with Rietveld analysis considering phases with partial or no known crystal structure [2]. The results showed that selective dissolution results in about 10% overestimation of the amount of unreacted fly ash and slag in hydrated cement paste in comparison with the other methods, but it provides consistent results. Moreover, selective dissolution remains as one of the more universal methods due to its relatively low cost and low specialisation required.

The dilution caused by aggregates in concrete and mortar makes the precision of the selective dissolution method very low for these two materials. Therefore, the method is convenient for hardened cement paste only. Similarly, the precision of the method decreases proportionally with decreasing SCM content of the cement paste. Minimum SCM content of 20% is recommended for the application of the method [1].

Blended cement paste is cured for the period under investigation, and after that samples should be immediately prepared and tested for selective dissolution. If samples need to be stored for some time before testing,

hydration stoppage should be done accordingly, and an appropriate procedure can be found in [3].

The current recommendation offers two procedures for selective dissolution, to be applied respectively on siliceous fly ash and slag admixed cement paste, with the aim of quantifying the reaction degree of the SCMs. The main differences in both procedures are the type of acid solution and the contact time. The computation of the result considers the precipitation of different products after dissolution, which depends on the composition of the respective SCM. This recommendation aims to provide guidelines for the procedure to be applied. However, it does not suggest any advantage of this method over other methods to determine the degree of reaction of SCMs. For a comprehensive comparison of different methods, the reader can refer to [1, 2].

## 2 Selective dissolution

### 2.1 Preparation of samples

The hardened sample must be ground to dust for the application of selective dissolution. First, it is recommendable that the external layer of the sample is discarded to avoid influences of carbonation or leaching. For the case of samples shaped as flat discs, this can be achieved with the aid of grinding paper applied to all faces of the sample. It is also convenient that the hardened sample is not from the base and top of the original specimen, as these sections may show differences due to the casting procedure. The hardened sample is manually ground with mortar and pestle to a maximum size of 125  $\mu\text{m}$  immediately before selective dissolution is applied. No automatic grinding should be applied, as excessive grinding can increase the solubility of the SCMs and reduce the repeatability of the procedure. If powdered samples need to be stored for some days after grinding, they should be put in a desiccator under vacuum together with a dish with soda lime to mitigate carbonation.

Powdered samples are oven-dried at 105 °C for 1 h and weighed to 0.0001 g. Filter papers (with pore diameter less than 4  $\mu\text{m}$ ) must also be previously oven dried at 105 °C for 1 h, weighed to 0.0001 g and stored in a desiccator prior to filtering.

The acid dissolution in correspondence with the type of SCM in the powdered sample is then applied.



Values expressed per 100 g dried paste are converted to values per 100 g of anhydrous binder using the loss on ignition of the dry cement paste according to Eq. (1). It should be noted that this correction may add a source of error, as the raw SCMs have their own loss on ignition (even at temperatures below 600 °C) [4]. Therefore, when possible the correction should be made considering the thermogravimetric analysis of the raw SCM.

$$m_{100 \text{ g of anhydrous binder}} = \frac{m_{100 \text{ g of dry paste}}}{(1 - \text{loss on ignition})} \quad (1)$$

## 2.2 Procedure for dissolution with salicylic acid and hydrochloric acid for siliceous fly ashes

This selective dissolution method is based on the European technical report CEN/TR 196-4 [5], which was developed for the determination of the composition of unhydrated fly ash blended cements. The method can also be used to determine the content of unreacted fly ash in a hydrated sample. It should not be used for calcium rich fly ashes, as the high solubility of this type of raw material leads to inaccuracies and a high variation in the results [2].

An acid mixture is produced containing 41 mL concentrated hydrochloric acid (37 wt%,  $\rho = 1.19 \text{ g/mL}$ ) and 50 g salicylic acid, made up to 1 L with methanol. Then  $2 \pm 0.02 \text{ g}$  (with a precision of 0.0001 g) of the powdered sample is mixed with 200 mL of the acid mixture in a glass beaker using a magnetic stirrer (about 300 rpm) for 30 min. The formation of lumps should be prevented, and if necessary they should be broken up with a glass rod prior to stirring. Afterwards, the insoluble residue is filtered off using the pre-moistened filter paper. All the residue is transferred to the filter, and the inside of the glass must be carefully washed with methanol and transferred to prevent any loss of solids. Due to the evaporation of methanol, salicylic acid may precipitate. This can be recognised by the violet colour. The filter has to be washed with methanol until the filter is completely white. The filter with the residue is dried at 105 °C for 2 h and weighed with a precision of 0.0001 g to determine the weight of the residue by difference with the weight of the clean filter paper.

The residue contains the unreacted fly ash and some insoluble components of Portland cement (mainly sulphate). In hydrated samples, the sulphate bearing phases like ettringite or monosulphate are dissolved, but then sulphate re-precipitates as gypsum. In both cases, bassanite is formed in the drying process. To calculate the content of unreacted fly ash, it is absolutely necessary to determine the bassanite content in the residue. Usually, the sulphate content ( $\text{SO}_3$ ) of the residue is determined chemically e.g. with a carbon/sulphur analyser. Then the bassanite content is calculated by multiplying the obtained sulphate content with a factor of 1.813 (based on the molecular weight). This computation is based on the premise that all the  $\text{SO}_3$  in the residue forms bassanite.

It is also possible to determine the bassanite content with other methods, like X-ray diffraction, but it has to be considered that the amount of the residue is quite small, especially for low fly ash contents. In any case, it is recommended to perform a determination in triplicate.

For hydrated samples with fly ash addition, it is necessary to investigate reference samples without fly ash to correct for small amounts of insoluble components of remaining clinker and possibly other cement components like blast furnace slag. Also, a correction for the fraction of soluble fly ash is possible by testing the pure fly ash with the same selective dissolution procedure (to verify the remaining amount after the attack). This correction can be disregarded ( $p = 1$ , especially for extended reaction periods) assuming that the soluble fly ash is reacting. The reaction degree of the fly ash in the hydrated cement paste can then be calculated according to Eq. (2).

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

$f$  mass fraction of fly ash in initial dry binder,  $p$  mass fraction of fly ash undissolved by salicylic acid + HCl.  $R_b$  mass of residue from the fly ash blended paste in g/100 g anhydrous binder.  $R_{\text{PC}}$  mass of residue from the OPC paste in g/100 g anhydrous binder.  $b$  mass of bassanite formed from 1 g of  $\text{SO}_3 = 1.813 \text{ g}$ .  $S_b$  mass of  $\text{SO}_3$  in fly ash blended paste residue in g/g of residue.  $S_{\text{PC}}$  mass of  $\text{SO}_3$  in OPC paste residue in g/g of residue.



### 2.3 Procedure for dissolution

with EDTA + TEA + DEA for blast furnace slag

This selective dissolution method is also based on the European technical report CEN/TR 196-4 (2007) and similar to the procedure proposed in [6].

A mixture of 250 mL of triethanolamine (TEA) and 500 mL of distilled water is produced, where 93 g of EDTA is dissolved, and then 173 mL of diethylamine (DEA) is rapidly added. Finally, the mix is completed with water up to 1000 mL. This solution is to be used within 1 month. For the dissolution of the sample, 50 mL of the buffered solution is put into a beaker and diluted with water to approximately 800 mL. While the solution is continuously stirred (about 300 rpm) and maintained at 20 °C,  $0.5 \pm 0.02$  g (with a precision of 0.0001 g) of powder sample is spread onto the surface preventing the formation of any agglomerate. Stirring is continued for 120 min. Afterwards, the insoluble residue is filtered off using a previously weighed and moistened filter paper (with mean pore diameter less than 4  $\mu\text{m}$ ) by applying suction (not lower than 250 mmHg). The stirrer and the beaker are carefully washed with water, and any adhering solid is detached and transferred using a glass rod with a rubber end. The residue is washed five times with 10 mL of water. The filter with the residue is dried at 105 °C for 1 h and weighed with a precision of 0.0001 g to determine the amount of the residue by subtracting the weight of the clean paper.

The reaction degree of the slag in the hydrated paste considering a correction due to precipitation of hydrotalcite-like phases within the collected residue is computed similarly to the procedure in [7], according to Eq. (3). The term hydrotalcite-like phases is preferred as pure hydrotalcite has the chemical composition  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$ , but the compound actually involved in this precipitation process contains interlayer  $\text{CO}_3^{2-}$  and a ratio Mg:Al varying between 2:1 and 3:1 [6]. The correction for the soluble fraction of slag can be disregarded ( $p = 1$ ) for long term reaction periods when considering that this fraction is reactive and will not remain unreacted in the mature sample.

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

$f$  mass fraction of slag in initial dry binder.  $p$  mass fraction of slag undissolved by EDTA + DEA + TEA.  $R_b$  mass of residue from the slag blended paste, in g/100 g of anhydrous binder.  $R_{\text{PC}}$  mass of residue from the OPC paste, in g/100 g of anhydrous binder.  $h$  mass of dried hydrotalcite formed from 1 g of MgO in the slag glass = 2.35 g for pure hydrotalcite (with Mg:Al = 3:1).  $M_s$  mass of MgO in the slag glass, in g/100 g slag.

### 3 Considerations and interpretation of results

The dissolution of raw cement, slags, fly ashes and the neat PC paste is carried out to determine the undissolved residue of these materials, which in the perfect case should be zero for the portland cement and its paste and 100 wt% for the SCMs. This is not the case, and although corrections for the incomplete dissolution of some components are included, some uncertainties related to these corrections are a source of error. PC pastes have shown a residue of less than 1% for the EDTA + DEA + TEA solution, whereas a residue of about 5–10% can be expected for the salicylic acid + HCl solution [8]. Both ranges are acceptable. The results given in [2] show that only 70–80 wt% of calcareous fly ash remained undissolved after the attack with salicylic acid + HCl, which makes the method unacceptable for the determination of the degree of reaction of this type of fly ash. The residue of slag can be rather low, around 90 wt%, but still acceptable. It is recommended that these selective dissolution methods are not applied to SCMs with a solubility ratio higher than 10%.

For the determination of the mass with respect to the anhydrous binder, the mass of sample should be corrected by the loss on ignition. Here, loss of weight at temperatures over 600 °C will be partly due to decarbonation whenever the constituent OPC contains limestone in its composition. Also Fe and unburnt carbon in unreacted fly ash, and S in unreacted slag, might cause weight variations during calcination of the blended paste [4]. Considering these contributions on the basis of the thermogravimetric analysis of the SCM in question will improve the precision of the method. The loss of bound water in the range 600–950 °C is minimal, and it is advisable to disregard it when there a possibility that the sample contains



carbonates. Then, the error connected with the release of CO<sub>2</sub> can be reduced if the loss on ignition for the temperature interval 105–600 °C instead of 105–950 °C is considered in Eq. (1). More reliable results can be obtained if this information is acquired by TGA instead of a plain loss on ignition.

Triplicate results should be obtained for each sample in order to obtain a reliable average result.

**Acknowledgements** The authors wish to present their special thanks to Ruben Snellings and John Provis for their comments on the draft of this recommendation. The fruitful discussion held with other members in RILEM TC 238-SCM is also appreciated.

#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

#### References

1. Scrivener KL, Lothenbach B, De Belie N, Gruyaert E, Skibsted J, Snellings R, Vollpracht A (2015) TC 238-SCM: hydration and microstructure of concrete with SCMs—state of the art on methods to determine degree of reaction of SCMs. *Mater Struct* 48(4):835–862
2. Durdzinski PT, Haha MB, Bernal SA, De Belie N, Gruyaert E, Lothenbach B, Méndez EM, Provis JL, Schöler A, Stabler C, Tan Z, Villagrán-Zaccardi Y, Vollpracht A, Winnefeld F, Zajac M, Scrivener KL (2017) Outcomes of the RILEM round robin on degree of reaction of slag and fly ash in blended cements. *Mater Struct* 50:135
3. Snellings R, Chwast J, Cizer Ö, De Belie N, Dhandapani Y, Durdzinski P, Elsen J, Haufe J, Hooton D, Patapy C, Perebatova O, Santhanam M, Scrivener K, Snoeck D, Steger L, Tongbo S, Vollpracht A, Winnefeld F, Lothenbach B (2017) TC 238-SCM: hydration stoppage methods for phase assemblage studies of blended cements—results of a round robin test. *Mater Struct* (submitted)
4. Bernal SA, Juenger MCG, Ke X, Matthes W, Lothenbach B, De Belie N, Provis JL (2017) Characterization of supplementary cementitious materials by thermal analysis. *Mater Struct* 50:26
5. CEN/TR 196-4 (2007) Methods of testing cement - Part 4: Quantitative determination of constituents. CEN European Committee for Standardization, Brussels
6. Lumley JS, Gollop RS, Moir GK (1996) Degrees of reaction of the slag in some blends with portland cements. *Cem Concr Res* 26(1):139–151
7. Luke K, Glasser FP (1987) Selective dissolution of hydrated blast furnace slag cements. *Cem Concr Res* 17(2):273–282
8. Durdzinski P, Haha MB, Bernal SA, De Belie N, Gruyaert E, Lothenbach B, Provis JL, Schöler A, Stabler C, Tan Z, Vollpracht A, Winnefeld F, Villagrán-Zaccardi YA, Zajac M, Scrivener KL (2016) Outcomes of the RILEM round robin on degree of slag and fly ash in composite cements. In: Proceedings of the international RILEM conference on materials, systems and structures in civil engineering—segment on concrete with supplementary cementitious materials, pp 293–297. ISBN 978-2-35158-178-0