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NEWSLETTER

Contents

Next ECRA events:

■ Cement and Admixtures
22 October 2015

■ Application of X-ray diffraction analysis
4–5 November 2015

Effects of superplasticizing admixtures used with blended cements

Significance of the BET specific surface and readily soluble cement constituents

Superplasticizers are key ingredients in modern concretes. Most of the superplasticizers are based on polycarboxylate ether. They improve the workability of concrete and have a positive impact on the concrete properties such as compressive strength and durability. The effect of these admixtures is strongly influenced by the specific surface of the cement constituents and readily soluble cement components.

Polycarboxylate ethers (PCEs) are copolymers of mostly polyether side chains grafted to a polycarboxylic main chain. Typically, the main chain is negatively charged in the alkaline cement paste's pore solution. Via the negative charges, PCEs adsorb on positive surfaces competing with sulphate ions. The uncharged side chains of the sorbed PCEs tangle into the pore solution and disperse the particles by steric hindrance.

Practical experience has shown that in unfavourable conditions the same type and quantity of superplasticizer in combination with different cements can lead to incompatibility reactions. This can result in an undesired consistency loss, over-fluidification of the concrete, sedimentation, retardation of cement hydration or delayed strength development.

The material parameters of blended cements influencing the mode of action of PCEs have therefore been determined. The investigated cements contained the same clinker and sulphate carrier and a systematic variation of the type and proportion of the additional main constituent.

Cements with limestone or granulated blastfurnace slag

Increasing proportions of limestone or granulated blastfurnace slag (GBFS) in the cement changed the ionic composition of the cement paste's pore solution significantly. In particular, the alkali and sulphate ion concentrations decreased virtually linearly due to substitution of the clinker (readily soluble alkali sulphates) by initially insoluble limestone or amorphous GBFS particles. Due to the reduced alkalinity of the pore solution, the solubility of calcium ions and therefore its concentration increased. In particular, the reduced sulphate concentration and the increased calcium content shifted the zeta potential of the cement paste, as a measure of the particle's surface charge, from weak negative to slight positive values. As a result of the reduced sulphate concentrations and the more positively charged surfaces, in particular a less negatively charged PCE for ready-mixed concrete adsorbed to a greater extent, compared to Portland cement.

With an increasing proportion of limestone or GBFS in the cement, the corresponding cement paste could be plasticized more effectively with smaller quantities of PCEs due to the reduced amount of initial hydration phases with their large specific surfaces. The quantity of PCEs needed for the maximum plastification of cement paste (saturation dosage) fell with increasing clinker substitution (**Fig. 1**). At the same substitution level, the saturation dosage increased with the BET specific surface of the cement constituents. This applied for the already mentioned PCE for ready-mixed concrete (PCE 11) as well as for a more negatively charged PCE for precast concrete (PCE 22). Added quantities of PCEs beyond the saturation dosage always led to sedimentation and/or retardation.

In combination with Portland cement, both PCEs exhibited considerable specific effects. PCE 11 maintained the consistency of the cement paste for a long time, whereas PCE 22 caused prompt stiffening. When the PCEs were used with blastfurnace cement CEM III/B, their specific effects had virtually disappeared. PCE 11 sorbed to a greater rate and the cement paste exhibited a distinct consistency loss because the pore solution had considerably lower sulphate ion content and the zeta potential was more positive. The clinker substitution and therefore the essentially reduced reactive surface resulted in a decreased sorption of PCE 22. Therefore, this superplasticizer provided a prolonged dispersing effect.
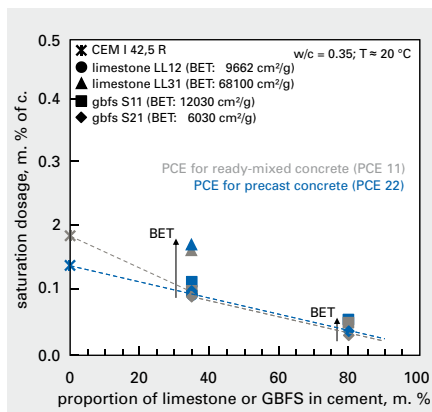

Fig. 1: Saturation dosage of cement paste depending on the superplasticizer as well as on the proportion of limestone or granulated blastfurnace slag in the cement.
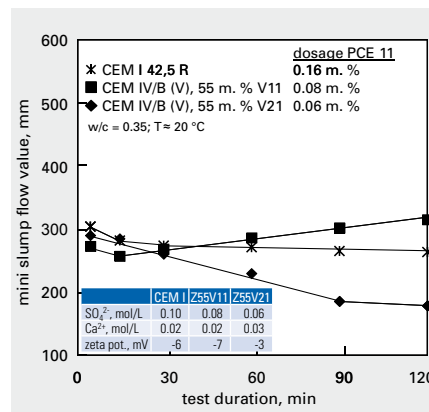

Fig. 2: Duration of plastification of superplasticizer depending on the type and proportion of fly ash in the cement.
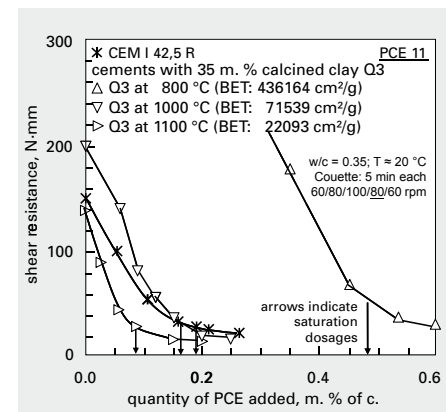

Fig. 3: Superplasticizer demand of cements with calcined clay depending on the clay's calcination temperature compared to Portland cement.

Cements with fly ash
Readily soluble fly ash constituents, e.g. alkali and sulphate ions, counteracted the previously mentioned dilution effect. Two siliceous fly ashes, one with more readily soluble sulphates (V11) and one with less (V21) were used to produce cements with 55 mass % fly ash (CEM IV/B (V)). In combination with both cements, the duration of plastification of the PCE 11 was tested. The results are shown in **Fig. 2**. On account of the virtually unchanged concentration of sulphate ions in the pore solution of the cement with V11 (Z55V11) compared to the Portland cement CEM I and the more or less identical zeta potential, the effect of PCE 11 used along with this cement was similar to that with Portland cement. Initially, PCE 11 remained for the most part

not adsorbed in the pore solution. Sorption took place over the test duration and the cement paste was plasticized. Used along with the cement with V21, the lower sulphate ion concentration and the less negative zeta potential led to greater sorption of PCE 11 and to an intensified stiffening of the cement paste (Fig. 2). Compared to the readily soluble constituents, the content of residual coke of fly ash (V11: 0.9 %, V21: 3.3 %) did not significantly influence the dispersing effect of the PCE.

Cements with calcined clay
The clays were calcined at the particular temperature necessary to meet the requirement of EN 197-1 of at least 25 mass % reactive SiO_2. The calcined clays exhibited hardly any

readily soluble constituents. Due to the flaky platelet particle structure, their BET specific surface was larger compared to e.g. fly ash. An increasing proportion of calcined clay in the cement resulted in an increased superplasticizer demand. Not decomposed, residual clay minerals in calcined clay further increased the cement's PCE demand. Cements with properly calcined clay (low BET specific surface) could be plasticized with almost comparable or even lower PCE dosages (**Fig. 3**). This emphasises the importance of adjusting the calcining conditions to the particular clay to reduce the water requirement and superplasticizer demand of the corresponding cement and thus enhance the workability of concrete.

Quantitative X-ray diffraction analysis in cement production control

Reliability, precision and robustness of fully automated XRD with Rietveld analysis

Quantitative X-ray diffraction analysis (QXRD) can be used to determine the phase composition of clinker and cement. However, its implementation into the quality control in cement production as an automated analytical process, including sampling, preparation, and evaluation does not allow for a validation of each single measurement. On the other hand, the plant operator requires reliable phase determination with good reproducibility, taking into account challenges such as production fluctuations or the quantification of cements with partially amorphous main constituents. While QXRD is well established in some cement plants as a crucial operational tool, many cement producers do not yet take advantage of this fast and automatable measurement method. Sufficiently accurate QXRD could supplement or even replace reference tests as part of factory production control and third-party inspection.

Phase analysis with QXRD can be applied on numerous materials within the cement production process. Most common are analyses on

clinker samples which are suitable for this method as they usually consist of well structured, crystalline phases. The evaluated phase composition reflects the kiln feed mixture and the burning and cooling conditions. Raw materials like limestone are analysed as a main part of the raw meal or as main or minor cement constituents. Sulphate agents can be analysed despite their status of dehydration, and dusts to be fed back appropriately into the production process. Furthermore, the quantification of partially X-ray amorphous main constituents like slags or fly ashes can be achieved under special circumstances, so that even quite complex cement compositions can be evaluated with acceptable precision.

Preparation and measurement
For all kinds of comparative X-ray analysis on powder specimens, continuity in the sample preparation is of crucial importance. This is achieved by commercially available preparation robots which are implemented in auto-labs. But the preparation routine itself must be carefully defined. In contrast to XRF prepara-

tions where the highest milling grade is the optimum for the analytical precision later on, the preparation of XRD samples must take into account the structural decay of some weak or cleavable mineral phases like gypsum, anhydrite or calcite. In practice, the XRD measurements are thus performed on cement samples of the usual technical fineness.

Evaluation procedure
The data evaluation with Rietveld analysis software starts with a simulation of a diffraction pattern calculated from the crystal structures chosen in advance. By an automatic variation of predefined parameters the contribution of each phase is fitted to the measured pattern, until a best possible agreement between the calculated and the measured pattern is achieved. The quantitative phase composition is obtained as one of the refinement results, and is always normalised to 100 %. For the sake of the robustness of the evaluation, it could be advantageous to disregard accessory mineral phases, or to restrict the variation of structural parameters (e. g. crystallinity, lattice spacing) to avoid errors due to wrong overlay corrections. On the other hand, for some phases different crystal modifications or textures must be taken into account.

X-ray amorphous components like slags can be described using a pseudo-structure which fits the so-called "glass hump", caused by the non-crystalline slag in the diffraction pattern background. Regular plant and cement type-specific definitions
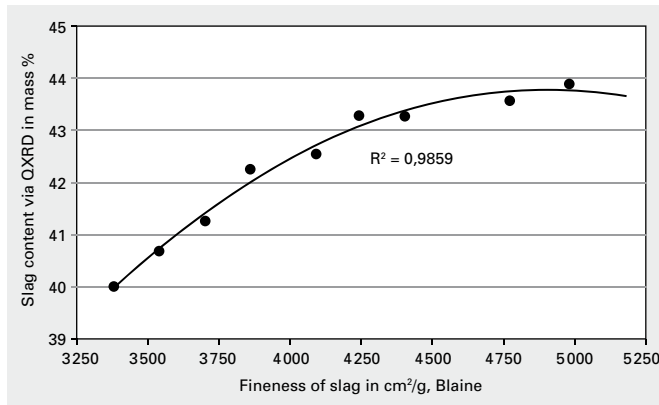
Fig 1: Slag content analysis via automated QXRD on laboratory cements with 40 mass % of slag of different fineness (evaluation adjusted on cement with coarse slag).
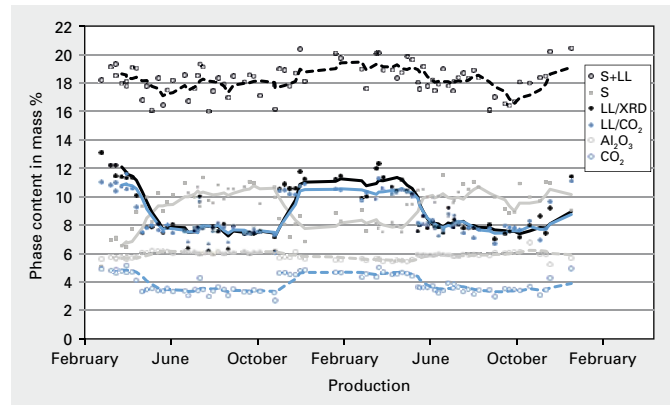

Fig 2: 2-year production of a CEM II/A-M (S-LL), comparison of main constituents and selected chemical parameters.

of the evaluation routine are necessary for reliable results.

For a comparative analysis, which is the common aim of production control, it is absolutely necessary to always use the identical evaluation routine. In this case, reproducibility scores as shown in **Table 1** for a CEM I can be achieved.

Each automated evaluation routine has to be validated when the source of the raw material changes. With limestone or slag the pre-defined routines might also work with the new material, in the case of fly ash an adjustment of the evaluation is usually required. The same applies to changing the relative fineness of the cement main constituents. At constant preparation, measurement and evaluation conditions, an increase of e.g. the slag fineness of 200 cm^2/g

acc. Blaine could raise the determined slag content by 0.5 to 1.0 mass % (**Fig. 1**).

Reliability in production

The suitability of automated QXRD is demonstrated by the application of pre-defined evaluation routines on production control data. In a research programme, data from extended production periods as well as from switchovers of cement types on a ball mill were analysed. In the latter case the point in time at which the requirements of the standard are met can be clearly defined.

By way of example, the X-ray diffraction results plotted in **Fig. 2** represent typical summer and winter mix formulations for a CEM II/A-M (S-LL) with seasonally alternating limestone powder and ground granulated blast furnace slag contents. The QXRD

corresponds very well to the chemical data of the specimens, e.g. the CO_2 or Al_2O_3 content. Even some phase content variations of less than 1 mass % could be correlated to changes in chemical composition.

QXRD in quality control

QXRD can accordingly be used in many cases for factory production control acc. EN 197-2 and could also be accepted by a third-party inspector. This does however pre-suppose a regular check-up of the processes on site by personnel experienced with the method and the performance of cross-validating tests with the standard reference method. Furthermore, agreement on and/or a factory-specific adaptation of the evaluation files for single cement types would be necessary in this case. Changes in the production processes generally cannot be accommodated. The use of different raw materials or production processes for one cement type may mean that third-party inspection via QXRD cannot be performed. As a general rule, the use of QXRD in third-party control requires close cooperation with the factory being inspected.

Table 1: Reproducibility of the preparation, measurement and evaluation of XRD analyses on Portland cement.

Phases	Reproducability							
	Preparation + measurement[1]				Measurement[2]			
	Mean	Min	Max	St.dev.	Mean	Min	Max	St.dev.
C_3S	66,1	65,27	66,91	0,64	65,2	64,52	65,57	0,40
C_2S	5,7	4,95	6,48	0,50	6,1	5,63	6,32	0,28
C_3A cub	2,5	2,40	2,64	0,11	2,5	2,42	2,65	0,10
C_3A orth	4,6	4,29	4,76	0,18	4,4	4,29	4,52	0,09
C_3A total	7,1	6,92	7,29	0,13	6,9	6,91	7,01	0,04
C_4AF	9,2	8,83	9,49	0,27	8,9	8,77	9,37	0,25
Free lime	0,6	0,51	0,71	0,08	0,6	0,55	0,68	0,05
Periclase	1,3	1,13	1,41	0,11	1,3	1,20	1,36	0,07
Quartz	0,3	0,22	0,39	0,06	0,3	0,24	0,39	0,06
Arcanite	0,9	0,82	1,03	0,08	0,9	0,78	0,93	0,07
Gypsum	0,1	0,06	0,12	0,02	0,1	0,07	0,12	0,02
Bassanite	2,5	2,23	2,77	0,20	2,6	2,47	2,77	0,11
Anhydrite	1,8	1,23	2,23	0,37	2,1	1,97	2,18	0,08
Calcite	3,0	2,74	3,23	0,23	3,1	3,02	3,23	0,09
Portlandite	0,6	0,21	1,05	0,36	1,1	1,00	1,15	0,06

[1] 6 samples, each in single measurement   [2] 1 sample, measured 10 times