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Estimation of the content of ground granulated blast furnace slag and different pozzolanas in hardened concrete

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HIGHLIGHTS

- Estimation of the content of GGBFS in hardened concrete.
- Estimation of the content of pozzolanas in hardened concrete.
- Compilation of methods for concrete analysis.

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ABSTRACT

Methods for estimating the content of ground granulated blast furnace slag (GGBFS), fly ash and other pozzolanas in hardened concrete were investigated including a selective dissolution procedure, a method based on scanning electron microscopy (SEM) combined with image analysis and a XRF method. The results reveal that the content of GGBFS in concrete can be estimated with all methods. The accuracy of the selective dissolution method can be increased by consideration of the dissolution behaviour of the respective aggregate. SEM investigations combined with image analysis additionally enable the estimation of the content of pozzolanas like fly ash or calcined clay.

1. Introduction

Supplementary cementitious materials (SCM) such as GGBFS or pozzolanas are widely used for the production of cements and concretes [1] as a part of the binder. In case of a reutilization, a damage or a defect of a structure a detailed analysis of the concrete including a quantification or estimation of the binder content and its composition is often desired or required [2]. Different methods for estimating the content of GGBFS or fly ash in cements, hardened cement paste, mortar or concrete have been reported before. Selective dissolution methods for GGBFS or fly ash [3–7] were especially used for determining the degree of hydration of these materials in hardened cement paste. The accuracy is assessed differently in these works and limits of these methods for determining the degree of hydration were summarized in [8]. Further methods based on gamma-ray-spectroscopy used for the quantification of fly ash [9,10], methods using XRF analysis [11–14], XRD after crystallization of GGBFS [15], XRD after a thermal treatment as an "inverse hydration" [16], XRD with Rietveld refinement and external calibration [17], electrical conductivity [18] and microscopic methods [19–21] were used. Most of these methods require either a calibration, a set aside sample of the specific SCM or of all concrete constituents for a retrospective analysis. Actually, in many cases no set aside samples are available especially months or years after the production of the respective structure. One solution for the determination of GGBFS in concrete without the need of such a set aside sample is based on scanning electron microscopy (SEM) with image-analysis or point-counting [22–24]. Although these methods are time consuming they have been found to be promising for the determination of GGBFS and to some extent for fly ash [17,23].

This paper discusses the applicability of a selective dissolution method, the XRF method based on XRF and SEM image analysis on hardened concretes in order to estimate the content of GGBFS, fly ash, a natural pozzolana (german rhenish trass) and a calcined clay. The influence of different aggregates on the estimation of

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the SCMs was studied. Advantages and limits of these methods have been worked out.

2. Materials and methods

2.1. Materials, mix design and sample preparation

For concrete production different blended cements were produced by an intensive mixing of an ordinary Portland cement (OPC) with different SCMs including GGBFS, natural pozzolana (german rhenish trass) and a calcined clay. The fly ash was mixed directly into different concretes as an addition. Three different aggregates (silicate rhenish gravel, crushed limestone, basaltic gravel) were used to study their influence on the different methods. The elemental composition of the materials measured by X-ray fluorescence (XRF) is given in Table 1. The content of CO_2 and H_2O was determined by IR-spectroscopy at 950 °C, the sulfide content according to EN 196-2 (iodometric titration) [25] and the content of Total Organic Carbon (TOC) according to EN 13639 [26]. The particle size distribution was determined with laser diffraction and RRSB parameters given in Table 2 calculated thereof.

The aggregates had a maximum grain size of 16 mm and a grading of A/B 16 as defined in standard DIN 1045-2 [27]. The basaltic gravel contained a quartz sand as fine fraction 0/2 mm.

In total 19 concretes (C1–C19) were produced by mixing the respective cement, fly ash as addition, aggregate and water. Different degrees of complexity of mix designs were selected as shown in Table 3. The concrete cubes of 15 cm edge length were stored under sealed conditions for 90 days.

At an age of 91 d the concrete cubes were prepared for analysis. Round about 5 kg of each concrete was crushed and dried at 105 °C. A representative sample of about 100 g was milled until passing completely the 90 μm sieve. Afterwards it was stored in argon atmosphere until analysis to prevent carbonation. This sample was used for the selective dissolution method and the XRF method.

Another part of each concrete was sawn in discs (35 × 50) mm of about 4 mm thickness, immersed in isopropanol for 7 d, dried in a desiccator over silica gel and embedded in a low viscosity resin as described in [24]. These discs were grinded and polished with diamond particles <0.125 μm. A minimum of two discs was prepared for each concrete.

2.2. Selective dissolution method

The selective dissolution method used is based on [28]. A dried, pulverized sample of a concrete is treated with a solution of disodium ethylenediaminetetraacetate (EDTA), triethanolamine (TEA) and diethylamine (DEA) which is largely able to dissolve clinker, the sulfate agent and calcareous fillers as well as the hydration products of different constituents like clinker, GGBFS and the other SCMs [3,4,24]. Ideally, the GGBFS fraction that has not yet reacted remains undissolved. Another sample of the pulverized concrete is then dissolved with dilute nitric acid (HNO_3) that additionally dissolves the non-reacted GGBFS. As the GGBFS fraction – which has not yet reacted – remains undissolved in the dissolving step with EDTA and is dissolved in the step with HNO_3 the unreacted GGBFS content is obtained from the difference between the two undissolved residues. Siliceous fillers, such as fly ash, or silicate based aggregates remain undissolved. In order to calculate the GGBFS content originally contained in the cement it is therefore necessary to know or estimate the dissolution behaviour of the hydrated GGBFS which is often associated with the degree of hydration. Various works have shown that the degree of dissolution of hydrated GGBFS at ages of 28 to 360 days is in the order of 40–60% [3,24]. The GGBFS content and the degree of dissolution of the GGBFS cannot be determined simultaneously with the selective dissolution method therefore an average degree of dissolution (*DD*) of the GGBFS of 50% was assumed initially for this work. The correlation between the degree of selective dissolution of a GGBFS and its degree of hydration is critically discussed in [8]. However, for an estimation of the original content of GGBFS only the degree of dissolution of a hydrated GGBFS is of interest, not the real degree of hydration. In order to relate the GGBFS content to the cement, the cement content (*Z*) was determined on the basis of DIN 52170-2 [29] using the insoluble residue in HNO_3 instead of an insoluble residue in diluted hydrochloric acid (HCl, 1:10). The GGBFS content is therefore calculated as shown in Eq. (1).

$$GGBFS = \frac{1.05^{*}[IR_{concrete,EDTA} - IR_{concrete,HNO3}]}{(1 - DD)^{*}Z} \quad (1)$$

with:

IR = insoluble residue
DD = degree of dissolution
Z = cement content

Table 1
Composition and insoluble residues of the concrete constituents.

Parameter wt.-%	OPC	SCM					Aggregate		
		GGBFS	FA	LL	Trass	CC	SG	CL	BG
CO_2	0.31	0.07	0.15	38.29	0.45	0.23	0.23	43.44	0.54
H_2O	0.38	0.09	0.21	0.85	6.11	0.69	0.95	0.30	1.42
SiO_2	22.1	35.75	50.5	7.91	55.46	58.78	90.26	1.43	54.00
Al_2O_3	3.94	10.96	26.38	2.25	17.45	23.13	3.61	0.20	8.58
TiO_2	0.19	1.03	1.24	0.09	0.95	1.07	0.18	0.01	1.87
P_2O_5	0.14	0.02	0.53	0.09	0.2	0.15	0.05	0.02	0.61
Fe_2O_3	1.42	0.43	8.13	0.98	5.91	8.05	1.73	0.20	8.38
Mn_2O_3	0.05	0.26	0.06	0.03	0.26	0.1	0.02	0.05	0.20
MgO	0.77	4.18	1.56	3.99	2.21	1.8	0.33	0.55	7.02
CaO	66.07	44.45	3.98	43.82	3.7	2.41	0.44	53.95	11.74
SO_3	3.2	0.01	0.37	0.4	0.14	0.06	0.01	0.10	0.17
K_2O	0.59	0.45	2.36	0.77	4.68	3.71	0.84	0.03	1.84
Na_2O	0.25	0.22	0.85	0.1	2.78	0.55	0.19	0.06	2.12
Sulfide	–	1.39	–	–	–	–	–	–	–
TOC	–	–	3.9	0.082	–	–	–	–	–
IR (EDTA)	0.8	96.8	92.03	27.71	94.17	94.34	96.8	2.7	96.5
IR (HNO_3)	0.53	0.07	89.75	12.68	81.92	92.83	98.3	1.8	75.6

OPC = Ordinary Portland Cement, GGBFS = Ground Granulated Blast Furnace Slag, FA = Fly Ash, LL = ground Limestone, Trass = natural Pozzolan, CC = Calcined Clay, SG = Siliceous gravel, CL = Crushed Limestone, BG = Basaltic gravel with quartz sand, IR = Insoluble residue.