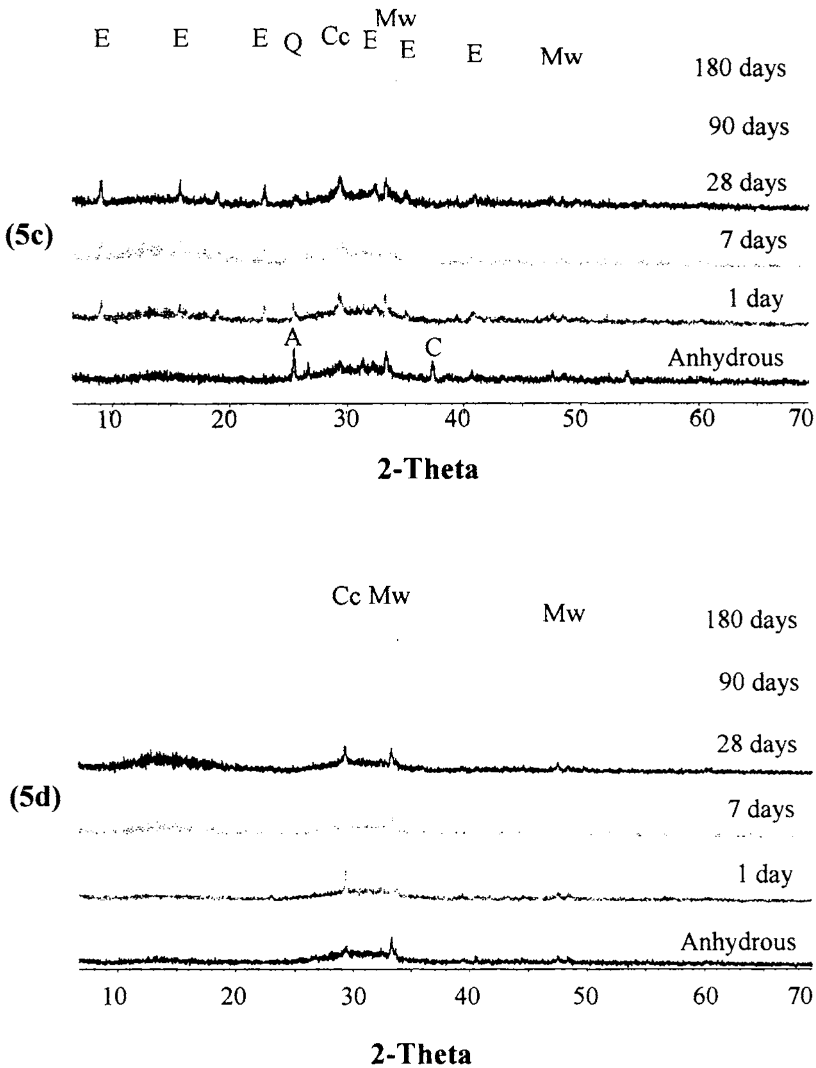

Figure 5. (Continued)
XRD patterns for anhydrous and hydrated blends of CFBC ash and GVBF slag (a): 25%A1/85%GS, (b): 15%A2/85%GS, (c): 15%A3/85%GS and (d): 100%GS
E: ettringite, Q: quartz, Cc: calcite, Mw: Merwinite, A: Anhydrite, C: CaO

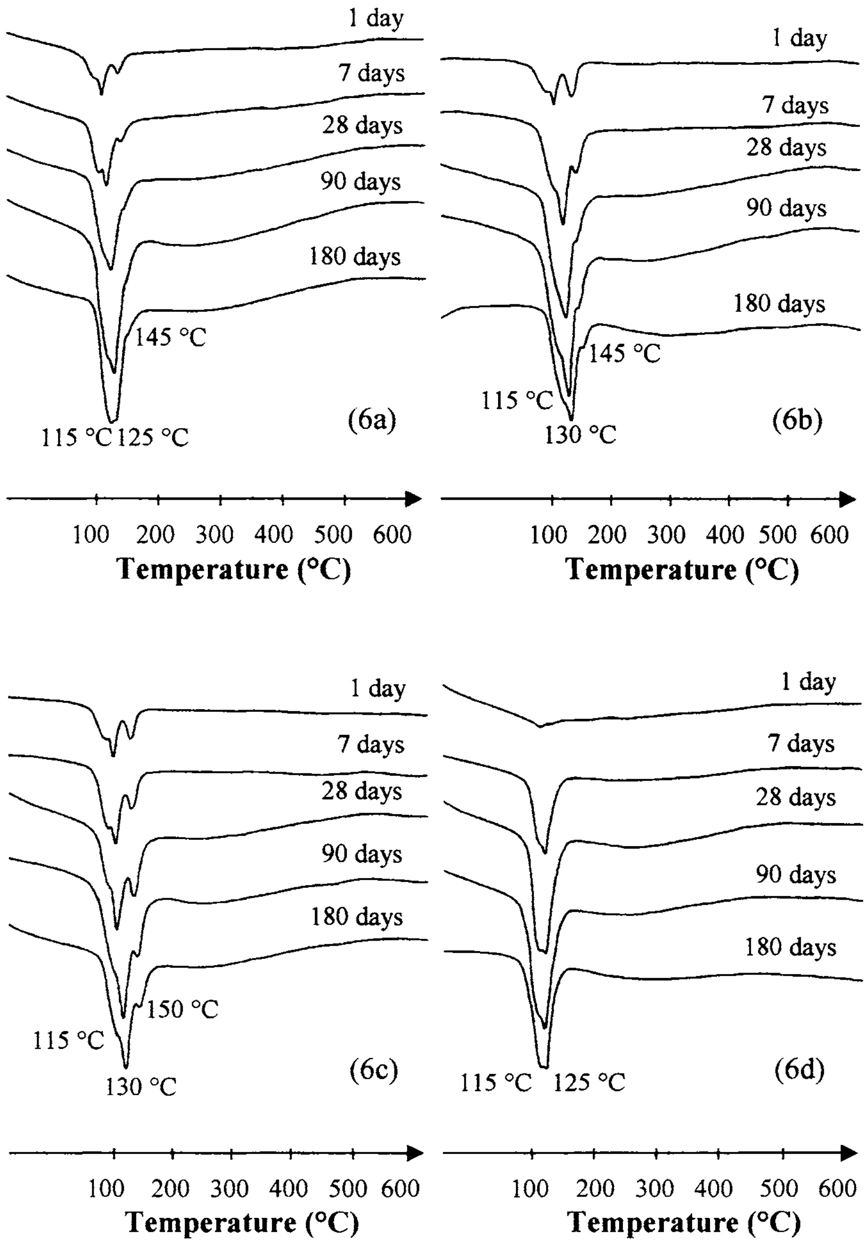

Figure 6.
DTA diagrams for hydrated blends of CFBC ash and GVBF slag
(a) 25%A1/85%GS, (b) 15%A2/85%GS, (c) 15%A3/85%GS, and (d) 100%GS

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Influence of Different Secondary Raw Materials on the Granulated Blast-Furnace Slag Reaction

by W. Brameshuber and P. Schröder

Synopsis: For the practical use of granulated blast-furnace slag as a clinker substitute, the addition of an activator is neccessary, in order to ensure that a sufficient early and ultimate strength will be reached. Up to now, portland cement has been the most common type of activator for granulated blast-furnace slag. The addition of portland cement leads to the activation of the granulated blast-furnace slag either on an alkaline or, to a minor extent, on a sulphate basis. Materials which prevent the obstruction of the latent hydraulic reaction by a close gel layer of reaction products work as an activator.

In this paper, the influence of different fine-grained additives, e. g. fly ash or cement kiln dust, on the granulated blast-furnace slag reaction and the strength development is discussed. The investigations showed that it is basically possible to manufacture composite cement with a high content of granulated blast-furnace slag by using industrially by-products. These cements shows particularly a higher early strength than the reference cement dependent on the composition respectively to the addition. The reactivity of the blast-furnace slag is strongly influenced by the chemical composition of the addition or activator but also by the mineralogical and chemical composition of the blast-furnace slag.

Keywords: activator; cement paste; composite cement; granulated blast-furnace slag; hydration; strength development; supplementary cementing materials

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INTRODUCTION

In the manufacturing process for iron ore, blast-furnace slag occurs as an industrial by-product. The molten slag is granulated with the aim of producing a high-quality product. Ordinary granulated blast-furnace slag has a high glass content, enabling the latent hydraulic reaction to take effect. This means that water-insoluble reaction products (e. g., calcium silicate hydrate) will form when water is added. In 1997, Germany produced 7.0 million tonnes of blast-furnace slag, of which 3.5 million tonnes per year were granulated to produce blast-furnace slag cement (1). For more than 100 years, granulated blast-furnace slag has been used as a binder in metallurgical cement. The use of granulated blast-furnace slag as a replacement for clinker is interesting from an economic and environmental point of view. In particular, the emission of CO_2 is reduced. For use as a cement additive, the granulated blast-furnace slag usually has to be ground to at least 400 Blaine (2).

An important requirement for granulated blast-furnace slag quality exists with regard to strength development in concrete. The granulated blast-furnace slag reacts more slowly than portland cement clinker, as a result the strength development of concrete slows down as the granulated blast-furnace slag content increases. The reactivity of granulated blast-furnace slag is usually quantified by the relative compressive strength of mortar (cement with granulated blast-furnace slag in comparison to a portland cement). The initial reactivity of the granulated blast-furnace slag in portland slagcement or in blastfurnace slag cement depends on the chemical/mineralogical composition of the portland cement clinker. Subsequently, it may be enhanced by the addition of fine-grained additives, e. g., fly ash or burned mineral matter such as cement kiln dust (3). The effectiveness of the fly ash is essentially based on its function as a nucleation sites. In contrast, cement kiln dust activates granulated blast-furnace slag predominantly on an alkaline basis. Cement kiln dust essentially acts in the same manner as portland cement, since it is very similar to this binder in terms of its chemical/mineralogical composition.

SCOPE

Granulated blast-furnace slag is generally used in cement production as an interground cement additive for the production of portland and blast-furnace cements. At present, the addition of fly ash or cement kiln dust to enhance the reactivity of granulated blast-furnace slag is only possible via the secondary constituents. Consequently, only small components can be used, up to a maximum of 5 % by mass. However, the draft standard DIN EN 197-1 (1998) provides for the production of composite cements with granulated blast-furnace slag and fly ash (4). The permissible granulated blast-furnace slag component is 50 % by mass, which means a reduction in the portland cement content. The use of such composite cements would reduce the volume of portland cement production. This will help to conserve the natural resources that are required to produce cement, while at the same time CO_2 emissions would also be reduced. In addition to the advantages pertaining to the production process, the composite cements also offer improved workability and durability, which means that the effectiveness of these cements in concrete is greater than that of conventional cements (5).

Table 1 shows the respective shares (in percent) of the total domestic delivery volume for the various types and strengths classes of cement from Germany in 1999 (6). In contrast to other European countries, in Germany the proportion of the total delivery volume constituted by portland cement is markedly higher than the shares of the other cement types. The total domestic delivery volume stood at around 33.8 million tonnes in 1999.

By reference to data in relevant literature, it was established that fly ash is fundamentally suitable for use as an interground cement additive in blast-furnace cements which are rich in granulated blast-furnace slag (content of granulated blast-furnace slag > 60 % by mass) (7, 8, 9). In Germany, fly ash is used solely as a concrete additive (10). The positive effect of fly ash on the course of the hydration process is attributed primarily to the rheological action, the physical filler effect, and the pozzolanic reactivity.

Cement kiln dust constitutes an effective agent to activate granulated blast-furnace slag. The chemical composition of this by-product of the cement production process corresponds essentially to that of the manufactured portland cement, but is characterised by high levels of calcium oxide, chloride and alkali content. Due to its varying chemical composition, which depends on the initial input materials for the cement production process, the kiln plant employed at the cement works, and the point at which it is recovered during cement production, cement kiln dust is used in Germany solely as a minor component (5 % by mass) produced in the cement manufacturing process.

EXPERIMENTAL APPROACH

General

Experiments were carried out at the Institute for Building Materials Research (ibac) using composite cements produced at the Institute, with the aim of reducing the portland cement content via the addition of interground granulated blast-furnace slag in combination with fly ash, cement kiln dust, or silica dust. In order to investigate the effectiveness of the different interground additives (fly ash, cement kiln dust and silica dust) on granulated blast-furnace slag, the strengths were determined on hardened cement paste specimens up to an age of 91 days. The reactivity of the granulated blast-furnace slag was additionally determined by means of thermogravimetric analysis on selected mixtures.

Materials

Two granulated blast-furnace slags of identical fineness and different chemical/mineralogical composition were selected for the experiments. The granulated blast-furnace slags differed in terms of glass content, as it is known that the glass content or the proportion of crystalline constituents influences the reactivity of granulated blast-furnace slag (11). Microscopy revealed granulated blast-furnace slag 1 to have a glass content of about 98.6 vol.-% and granulated blast-furnace slag 2 to have a glass content of about 94.8 vol.-%. X-ray diffraction analysis identified the crystalline constituents of granulated blast-furnace slag 2 to be Bredigite ($CA_{14}Mg_2(SiO_4)_8$) and calcium silicate ($CaSiO_4$). For granulated blast-furnace slag 1 no crystalline constituents could be verified by using the X-ray diffraction analysis (peak was below the detection limit), Fig. 1.

The investigated portland cement (CEM I 32.5) and the cement kiln dust originate from a German cement works. The cement kiln dust is a bypass dust, which on the basis of its chloride content can be classified as possessing a medium level of contamination (Table 2). The permissible chloride content for cements is stipulated in DIN EN 197 (4) at ≤ 0.10 %, therefor, a maximum of 5 % by mass of cement kiln dust can be added for production of the composite cements. A fly ash from a dry bottom furnace approved as a concrete additive in accordance with German standard DIN 1045 (12) (low calcium fly ash, class F according to ASTM C 618 (13)) was also included in the test program. In order to assess the effects of the various intergrinding materials (fly ash and cement kiln dust) on the reactivity of the granulated blast-furnace slag, a silica dust was used as an inert material. The chemical compositions and selected physical properties of the raw materials are summarized in Table 2.

Mixture proportions

Table 3 shows a summary of the produced composite cements. In order to use the largest possible proportion of secondary raw materials, all the composite cements were produced using 75 % by mass of granulated blast-furnace slag. The proportion of fly ash and cement kiln dust varied between 5 and 10 % by mass. The proportion of portland cement fell accordingly from 25 % by mass to 20 or 15 % by mass.

In order to ensure good workability, a water-cementitious material ratio (w/cm) of 0.50 was used for all the mixtures. The mixing process was carried out in accordance with the German standard DIN EN 196-1 (14).

Specimen production

The compressive strength was determined on cylindrical hardened cement paste specimens. The cement paste with a w/cm of 0.50 was poured into PVC cylinders measuring (d = 25 mm, h = 100 mm), sealed air-tight with a silicone plug and rotated for 48 h in order to prevent segregation of the cement paste, before setting. After removal from the mold, the specimens were sawn to a height of 75 mm and shrink-wrapped in polyethylene-foil. This was necessary because cement paste specimens are particularly susceptible to carbonation and drying out.

Residual pieces from the compressive strength test were used to determine the reactivity. In order to dispel the water which was not chemically bound and, thus, to stop the hydration of the cement paste at the given time, the material was placed in isopropanol for 24 h. The supernatant liquid was decanted and the crushed specimen was dried at 105 °C until constant mass was attained. After this procedure the coarsely crushed specimen was then ground to a grain size of d < 0.125 mm. The dried powder was kept in a sealed container until the measurement process.

Test method

The compressive strength was determined on the above-stated cement paste specimens (d = 25 mm, h = 75 mm), which were shrink-wrapped in polyethylene-foil and before testing unwrapped, after 2, 7, 28 and 91 days. The loading rate was 10 N/s for the 2- and 7-day specimens and 100 N/s for the 28- and 91-days specimens.

The thermogravimetric analysis method (TGA) was used to determine the reactivity of granulated blast-furnace slag. The TGA method detects changes in the mass of a substance during heating due to thermal reactions. This generally involves the splitting-off of volatile substances, such as water or carbon dioxide (CO_2). In the temperature range from approximately 100 to about 700 °C the calcium silicate hydrate phases (CSH) will be continued drain. Between 400 and 500 °C the water becomes split off from the calcium hydroxide ($Ca(OH)_2$) in accordance with the following reaction equation:

$$Ca(OH)_2 \overset{\Delta T}{\Rightarrow} CaO + H_2O.$$

The information obtained from evaluating the thermogravimetric data, mainly the $Ca(OH)_2$-content and the water contained in the CSH-phases, provides an effective means of monitoring the reaction progress in the parallel cement and granulated blast-furnace slag hydration processes.

A TG apparatus from the METTLER company was used, consisting of an oven, a balance (TG 50), and a data acquisition unit (TC 10 A). In order to prevent the oxidation of certain substances and to discharge gaseous reaction products, the specimen is located in a nitrogen chamber during the analysis process. The measured data were transferred to a computer, where they were evaluated using the Institute's own software. The heating rate in all the tests was 10 K/min. The analysis program covered a temperature range from 30 to 894 °C. The specimen mass was about 50 mg.

RESULTS AND DISCUSSION

Influence of the granulated blast-furnace slag

Fig. 2 shows the development of compressive strength in the composite cements containing the various granulated blast-furnace slags in combination with 5 % cement kiln dust, fly ash and silica dust. The blast-furnace cement with granulated blast-furnace slag 2 (C20) possesses a compressive strength of 28.3 N/mm² at 28 d. By comparison, blast-furnace cement C10 with granulated blast-furnace slag 1 results in a compressive strength of 25.8 N/mm² at 28 d. A possible cause of the slightly higher compressive strength for C20 may be the higher alkalinity of granulated blast-furnace slag 2. As Table 2 shows, granulated blast-furnace slag 2 differs from granulated blast-furnace slag 1 in possessing a C/S ratio of 1.35. X-ray diffraction revealed a low level of crystalline content in granulated blast-furnace slag 2. According to (11, 15, 16), granulated blast-furnace slags with crystalline constituents possess higher reactivity than fully vitreous granulated blast-furnace slags, as the finely distributed crystal nuclei are capable of weakening the glass structure.

Replacing 5 % by mass of portland cement with cement kiln dust results in a marked increase in early strength in the composite cement containing 75 % by mass of granulated blast-furnace slag 2 (C23). The compressive strength rises from 4.6 to 11.4 N/mm² at an age of 2 d and from 14.9 to 23.9 N/mm² at an age of 7 d (Table 4). The positive influence of the kiln dust on reactivity can be attributed to the chemical/mineralogical composition of the cement kiln dust (Table 2). The high chloride content is able to accelerate hydration of the portland cement, while the formation of calcium hydroxide ($Ca(OH)_2$) and the release of alkalies lead to alkaline activation of the granulated blast-furnace slag. Overall, granulated blast-furnace slag 2 appears to possess higher reactivity in the early phase than granulated blast-furnace slag 1, on account of its crystalline constituents. At an age of 91 d, blast-furnace cement containing granulated blast-furnace slag 1 (C13) attains a compressive strength of 36.3 N/mm². It appears that the activation by the cement kiln dust does not affect the reactivity of granulated blast-furnace slag 1 until a later juncture.

Replacing 5 % of the portland cement content with fly ash does not produce any significant increase in compressive strength. Only at an age of 91 d did the compressive strength of composite cement containing granulated blast-furnace slag 2 (C21) rise compared with the reference mixture (C20), from 30.5 to 33.6 N/mm². In the early phase, the fly ash induces a so-called dilution effect. As expected, replacing 5 % of the portland cement contact with silica dust does not produce any increase in compressive strength. The compressive strengths of the cements containing granulated blast-furnace slag 1 and granulated blast-furnace slag 2 are on the same level.

Fig. 3 shows the compressive strengths of the composite cements 5 % by mass of cement kiln dust, fly ash and silica dust as a function of the hydrate water determined by means of TG. A linear correlation is revealed between the water from the CSH phases (hydrate water), from the granulated blast-furnace slag reaction, and the compressive strength. On the basis of the TG data documented in Table 5, a slightly lower hydrate water content was determined for all composite cements containing granulated blast-furnace slag 2 than for the composite cements containing granulated blast-furnace slag 1.