GLASS STRUCTURE OF GRANULATED BLAST FURNACE SLAG AND ITS REACTIVITY - A NEW APPROACH

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Introduction

World-wide ≈ 280 Mt/yr GBS are produced and for more than 130 years GBS is used as a cementitious material. Many approaches exist to evaluate the reactivity of glassy GBS in cementitious systems. Glass content, chemical composition, fineness, *etc.* have been considered. All approaches failed to define a suitable tool for judging an unknown GBS in a way that *e.g.* its strength contribution can be predicted. The reason is that the thermal history of the slag resulting as well from the blast furnace as from the granulation process, which is considered also to be very important,[1] is unknown. The question to be answered is whether any correlation between thermal history, "enthalpy content" and technical properties exists.

Methods

Glass properties

The direct measurement of the cooling rate is impossible. However, glassy material stores the information about prior cooling in its structure and a common way to define it is based on the fictive temperature (T_f) determination.

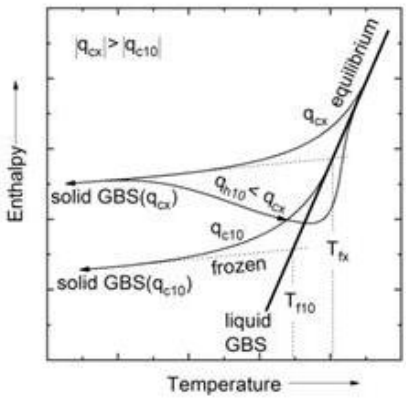

Figure 1: Schematic dependence of glass enthalpy on cooling and heating conditions;[2] q_{cx} is the fast cooling rate of wet granulation, q_{h10} is the standard heating rate of 10 K min^{-1} and q_{c10} is standard cooling rate of 10 K min^{-1}

Figure 1 shows that on cooling of the glass GBS from the equilibrium liquid state, the fictive temperature is equal to the physical temperature ($T_f = T$) and the system is in equilibrium. With decreasing temperature, however, the molecular mobility decreases while the viscosity of the melt increases and at one point the time required for relaxation becomes longer than the time that the melt spends at that exact temperature, the structure freezes in and the material deviates from the equilibrium and begins to form a solid glass ($T_f > T$). The fictive temperature depends on the cooling rate that the melt undergoes: a faster cooling leads to higher fictive temperature. Hence, the higher T_f, the stronger the system has departed from equilibrium. The glass transition temperature T_g, on the other hand, is a particular case of T_f. It is determined for the defined thermal history at a cooling rate of 10 K min^{-1} ($T_g = T_{f10}$ in Figure 1). Of course, T_g depends also strongly on the glass composition.

2 GBS with different chemistry (GBS 13: (C+M)/S = 1.18; GBS 14: (C+M)/S = 1.44) were investigated, in both cases as well as the original quenched GBS that exhibits higher T_f as the annealed GBS with lowered T_f. To anneal GBS, it was kept at 0.9 x T_g for 24 h in air in order to allow the relaxation of the glass and thus to eliminate the unknown thermal history derived from quenching and to lower T_f. As a result, the annealed GBS has a lower enthalpy content and it might have a lower reactivity, too. Ground GBS samples were analysed by the Hyperquenching-Annealing-Calorimetry (HAC) method[3] and T_g and T_f were determined. The first upscan was carried out on the quenched sample (unknown thermal history), whereas the second upscan was done on the sample which was relaxed and has a new thermal history of 10 K min^{-1} (standard cooling).

To calculate the original cooling rate q Equation (1) has to be used.

$$\log \eta(T_f) = K - \log q \qquad (1)$$

A critical point is to calculate the viscosity η at T_f where it is not to be measured but only to be calculated.[4]

Cementitious properties

To evaluate the cementitious properties of industrial and annealed GBS the slag was ground in a 10 kg ball mill to ≈ 4200 cm^2/g (Blaine). To stress the influence of GBS properties on the cementitious properties, blast furnace cements with 75 wt% ground GBS and 25 wt% clinker were tested according to GBS database of FEhS[5]. The total SO_3 content of the cements was 4.5 wt% adjusted by adding anhydrite and gypsum. The strength development has been investigated according to EN 196-1

(mortar prisms 40 x 40 x 160 mm, w/c = 0.50). Heat of hydration was measured for 7 days (cement lime, w/c = 0.50) using an isothermal calorimeter.

Results

Cooling rates

For GBS 14 Figure 2 shows the heat capacity curves as a function of temperature obtained from DSC measurements. The first upscan (left; red line 1) reveals the broad exothermic effect that is attributed to the release of the potential energy enclosed in the GBS during the granulation process. The second upscan (black line 2) of the standard cooled GBS exhibits no exothermic effects (since cooling rate equals the heating rate) and allows the fitting of the Maier-Kelley equation.[4,6] In case of the annealed GBS 14 (Figure 2, right) the first upscan and the second upscan matches in the sub-T_g range, but a larger overshoot at $T > T_g$ is evident, which indicates a lower T_f than that of the standard cooling.

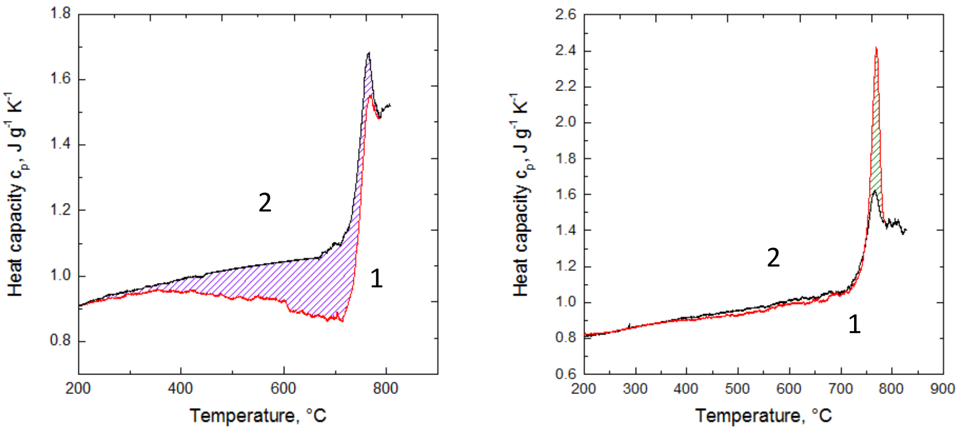

Figure 2: Heat capacity curves of GBS 14 after wet granulation (left) and after annealing at 0.9 x T_g for 24 h (right). The red line 1 represents the heat capacity of the first upscan, while the black line 2 represents the heat capacity of the second upscan after standard cooling at 10 K min^{-1}

The fictive temperature T_f of the wet granulated GBS 14 was 848°C, whereas T_g was 734°C. The T_f and T_g of the wet granulated GBS 13 are lower and are equal to 827°C and 721°C, respectively. Using 4 different $\eta(T)$ models, the viscosity at the fictive temperature $\eta(T_f)$ was determined. Finally, transformed Equation (1) was used to approximate the cooling rate q_{cx} for original and annealed GBS. The cooling rates are calculated to be in the range of 90 000 - 890 000 K s^{-1} depending on the model.

Cementitious properties

The glass content of the annealed GBS was unchanged (GBS 13b: 95 / 99 vol%; GBS 14: 99 / 98 vol%). The compressive strength is shown in Figure 3. It is obvious that

both cements with annealed GBS (bars 1 and 3) being minimised in its enthalpy content result in a significant lower compressive strength at all hydration ages being tested. For GBS 13b the effect after 2 days is very limited due to the general lower reactivity. For GBS 14 having as well a higher basicity as a higher alumina content also after 2 days the negative impact of the annealing procedure is considerable.

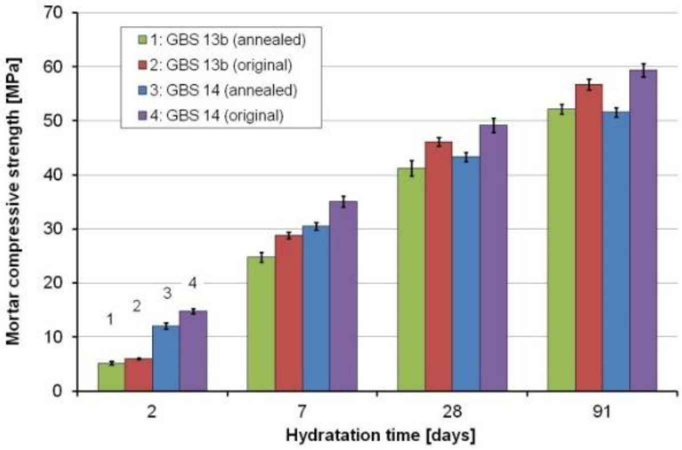

Figure 3: Mortar compressive strength acc. to EN 196-1 for original and annealed GBS

Summary

For the first time it was possible to verify that the thermal history of a GBS has really a significant impact on the technical properties of slag containing cements. As it can be expected from basic thermodynamic consideration an annealed GBS has a lower reactivity in the sense of heat of hydration and strength development compared to an industrial GBS. Thus, it allows the conclusion that a higher cooling rate during the wet or dry granulation process of a liquid blast furnace slag should result in a higher GBS reactivity.

References

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