

Rapid discrimination of the character of the water-cooled blast furnace slag used for Portland slag cement

T. ITOH

Chemistry Department, Miyazaki Medical College, University of Miyazaki, Miyazaki 889-1692, Japan
E-mail: titoh@fc.miyazaki-med.ac.jp

Recycling of blast furnace slag has been used for a long time in the manufacture of composite cement. Blast furnace slag makes a substantial contribution to the hydration product. It is of importance to determine the quality of the blast furnace slag added to cement based on “only one parameter” in a short period of time. In other words, we might be able to estimate the approximate strength of the concrete specimens made of slag cement several months in advance based on one parameter. A number of studies have been carried out to relate the character of slag and the properties of the concrete composite made of Portland slag cement [1–11]. Water-cooled slag is generally more effective for strengthening the concrete composite than air-cooled slag. In the present work, we have investigated the character of water-cooled blast furnace slag as an additive of Portland cement in order to reconfirm the equations proposed previously and to construct an equation for estimating the mechanical strength of concrete composites. We have prepared the concrete specimens using slag cement containing various kinds of slag with different chemical compositions and thermal history, and measured the compressive strength of the specimens.

Chemical compositions of each slag were analyzed according to JIS R-5202-19: Grained specimens were treated with perchloric acid, and the amounts of SiO_2 , Al_2O_3 and MnO were determined by gravimetric analyses, those of TiO and Fe_2O_3 were determined by UV/VIS spectrometry, and those of CaO and MgO were determined by means of chelatometry. The average chemical composition of the used slag was 34.8 (SiO_2), 14.7 (Al_2O_3), 0.8 (TiO_2), 0.25 (Fe_2O_3), 0.6 (MnO), 41.8 (CaO), 6.3 (MgO), 0.24 (Na_2O), 0.45 (K_2O) and 0.8 wt% (S).

The crystal species contained in the slag were found to be mostly melilite $((\text{CaO})_2(\text{Al}_2\text{O}_3)_2(\text{SiO}_2))$ and merwinite $((\text{CaO})_3(\text{MgO})(\text{SiO}_2)_2)$. These crystalline materials were synthesized and were mixed with slag in appropriate ratios to make calibration curves for X-ray diffractometry for the determination of the crystal content in the slag. Slag samples for microscopic observation were grained and sieved to obtain the sieve fraction between 62 and 105 microns. Slag powders thus separated were observed with a polarization microscope, and the total number of the particles and the number of the crystallized particles

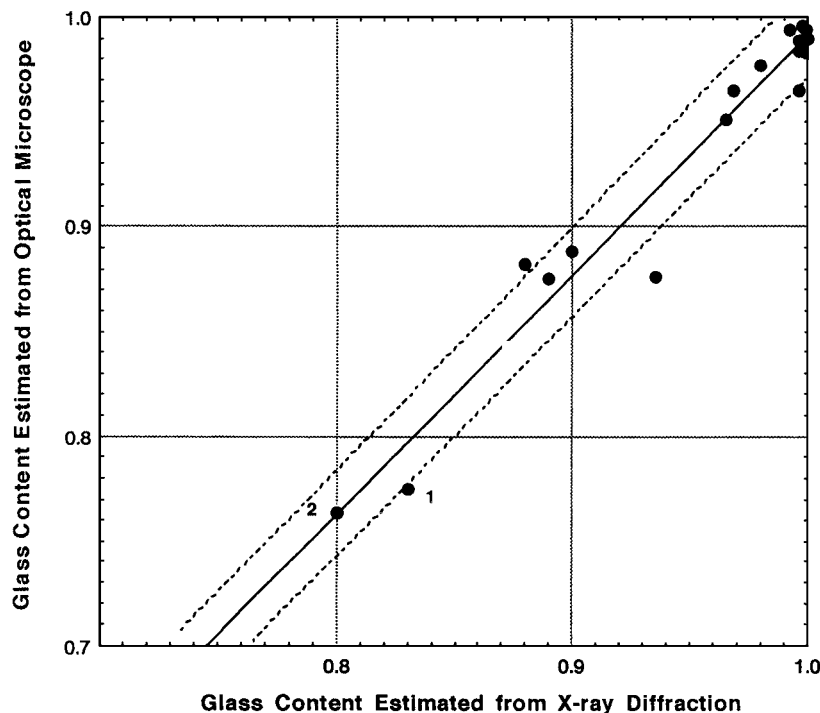


Figure 1 Relation between the glass content estimated from X-ray diffraction and optical microscope. For the determination of the glass content both air- (1 and 2) and water-cooled slag (others) were used.

were counted. In some cases melilite crystal tended to be misjudged as glass, while merwinite crystalline content tended to be over estimated, since the latter crystal is fibrous, spreads, and shows high refractive index and birefringence. The particles with crystal content over 30% were treated as crystallized particles, while those with crystal content below 30% were treated as non-crystallized particles. The counting was carried out for over 500 particles in the microscope field. The glass content, G ($0 < G < 1$), in this case was obtained by $G = (\text{the total particle number} - \text{the number of the crystallized particles}) / \text{the total particle number}$. As is shown

in Fig. 1, the correlation between G values obtained with X-ray diffraction and the optical microscope was satisfactory with the correlation coefficient (r) of 0.95. In both methods we can estimate the glass content of the slag within a few hours.

The concrete specimens were prepared in the following way. Each slag was milled until the blaine was $500 \pm 10 \text{ m}^2/\text{kg}$. The weight ratio for normal Portland cement:slag was kept at 1:1. The weight ratios for Portland slag cement:sand were kept 1:2, and 3 wt% gypsum (blaine $498 \text{ m}^2/\text{kg}$) was added. Compressive strengths, F_c , of the concrete specimens were measured

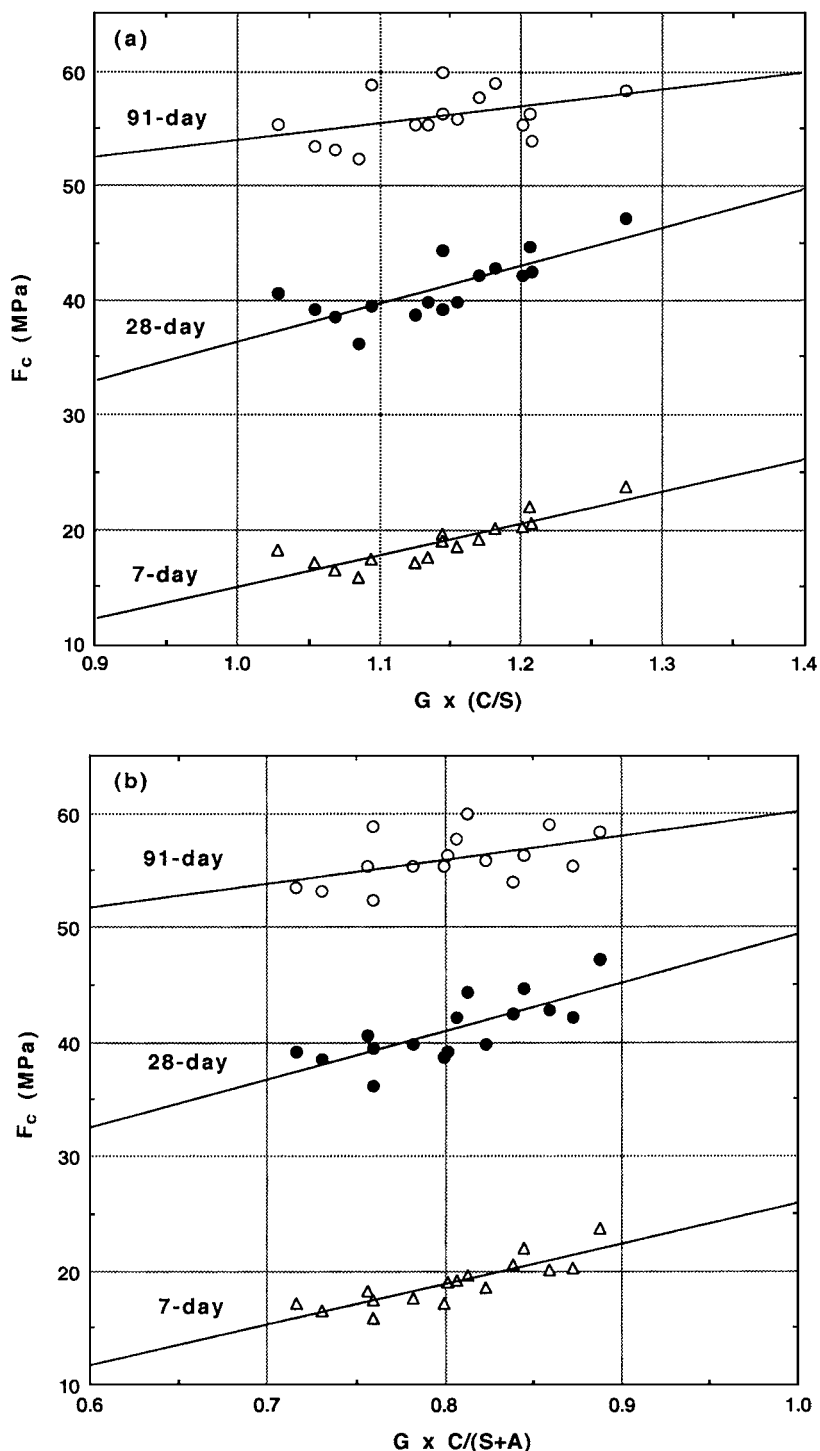


Figure 2 Compressive strengths of concrete specimens, F_c , plotted against $G \times [\text{CaO}]/[\text{SiO}_2]$ ($G \times (C/S)$) (a) and $G \times [\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3])$ ($G \times C/(S + A)$) (b). The F_c values for 7-, 28- and 91-day concrete specimens without slag are 19.5 (199), 37.5 (382) and 46.4 MPa (473 kg/cm²), respectively. Only water-cooled slag was used for the analysis.

according to JIS R5201-196: Slag cement pastes with a water/slag-cement weight-ratio of 0.65 were prepared to make concrete specimens of the size $0.4 \times 0.4 \times 1.6 \text{ dm}^3$, which were used for mechanical measurements.

We have investigated the relationship between various parameters of slag and the compressive strength of the concrete composites. Correlation coefficients between CaO content (wt%), [CaO], in slag and F_c of the composite are positive, while those between SiO₂ or Al₂O₃ content (wt%), [SiO₂] or [Al₂O₃], and F_c are negative. MgO content, [MgO] correlates positively with F_c for short period, but negatively for long period. It might be possible to relate chemical composition or basicity of slag with the mechanical strength, F_c , of the composite in a way such as $F_c = k_1[\text{CaO}] + k_2[\text{SiO}_2] + k_3[\text{Al}_2\text{O}_3] + k_4[\text{MgO}]$ or $F_c = k_1([\text{CaO}]/[\text{SiO}_2]) + k_2([\text{Al}_2\text{O}_3]/[\text{SiO}_2]) + k_3([\text{MgO}]/[\text{SiO}_2])$. In these treatments, however, the coefficients $k_1, k_2, k_3 \dots$ may vary depending on the quality of slag and cement used as well as other factors. Hence, we tried to relate the strength of the concrete composites and character of the slag using only one parameter, and finally we obtained the following expression that relates the character of the slag with the compressive strength of the concrete composite.

$$F_c \cong c_1 \times G \times [\text{CaO}]/[\text{SiO}_2] + c_2 \quad (1a)$$

$$F_c \cong k_1 \times G \times [\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3]) + k_2 \quad (1b)$$

The relation between the measured compressive strength and the value, $G \times [\text{CaO}]/[\text{SiO}_2]$ or $G \times [\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3])$, is shown in Fig. 2. The correlation coefficient between F_c and $G \times [\text{CaO}]/[\text{SiO}_2]$ is 0.63 for 7-day specimens, 0.51 for 28-day specimens and 0.27 for 91-day specimens, while that between F_c and $G \times [\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3])$ is 0.69 for 7-day specimens, 0.55 for 28-day specimens and 0.35 for 91-day specimens. The correlation between F_c and the parameter is not significant for 91-day specimens. However, it follows from Figs 2a and b that when the $G \times [\text{CaO}]/[\text{SiO}_2]$ value of the slag is over 1.1, addition of the slag is expected to strengthen the concrete composite to a certain extent. In the same way, when the

$G \times [\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3])$ value is over 0.8, addition of the slag is expected to strengthen the composite to a certain extent. It should be noted that we are using only one parameter such as $G \times [\text{CaO}]/[\text{SiO}_2]$. The implication of this parameter is simple, i.e., it is mainly the chemical composition ratio ($[\text{CaO}]/[\text{SiO}_2]$ or $[\text{CaO}]/([\text{SiO}_2] + [\text{Al}_2\text{O}_3])$) in the glass of the slag which contributes to the strengthening of slag cement. It is also possible to say that the character of slag depends in part on its thermal history where the slag produced under slower cooling conditions tends to form considerable crystalline phase and to deactivate the glass phase formed. Discrimination of an appropriate slag can be carried out in a day or so in an inexpensive way. This involves chemical analyses of a few elements and observation with an optical polarization microscope.

Acknowledgment

The author is grateful to Dr. Y. Ono for the advice in the initiation of this work.

References

1. S. YAMAUCHI, R. KONDO, *J. Ceram Soc. Jpn.* **59** (1951) 489. (In Japanese)
2. T. TANAKA, T. SAKAI and J. YAMANE, *Z-K-G.* **11** (1958) 50.
3. G. MASCOLO, *Cement Concr. Res.* **3** (1973) 207.
4. H. G. SMOLCZYK, *7th Int. Cong. Chem. Cement* **3** (1980) 1.
5. DEMOULIAN, P. GOURDIN, F. HAWTHORN and C. VERNET, *Proc. 7th Int. Cong. Chem. Cemento* **3** (1980) 89.
6. K. E. DAUGHERTY, B. SAAD, C. WEIRICH and A. EBERENDU, *Silicate Ind.* **4** (1983) 107.
7. R. YUAN, S. OUYANG and Q. GAO, *ibid.* **1** (1983) 3.
8. Y. MAEDA, H. NAGANUMA and T. HASIMOTO, *CAJ Proc. Cement and Concrete* **44** (1990) 180. (In Japanese)
9. K. M. SHARMA and S. C. AHLUWALIA, *World Cement* (1995) 74.
10. J. S. LUMLEY, R. S. GOLLOP, G. K. MOIR and H. F. W. TAYLOR, *Cement Concr. Res.* **26** (1996) 139.
11. N. Y. MOSTAFA, S. A. S. EL-HEMALY, E. I. AL-WAKEEL, S. A. EL-KORASHY and P. W. BROWN, *ibid.* **31** (2001) 899.

Received 10 June

and accepted 13 October 2003