



GLASS CONTENT INFLUENCE UPON HYDRAULIC POTENTIAL OF BLAST - FURNACE SLAG

by Rene Galibert

It is generally admitted that blast-furnace slags have hydraulic power that depends for one part on their chemical composition and for another on their microstructure. Most of the authors estimate that the vitreous structure is the controlling condition because the vitreous state makes possible and explains the reactions which would not be possible from crystallized material.

Liquid blast-furnace slags contain four major elements: CaO, SiO2, Al2O3 and MgO which during cooling combine to produce mineralogical compounds. The nature and proportions of these mineralogical compounds depend not only on those four constituents but also equally on less-known minor compounds, e.g., iron oxides, TiO2, sulfides, that can have a nucleator function and direct the crystallization toward one mineralogical compound rather than another.

R.H. Bogue has given in the book "The Chemistry of Portland Cement"1 equations that apply to different clinkers to determine their potential mineralogical composition from the chemical composition. Gourdin, from Ciments Francais Corporation, has suggested that the potential hydraulic powers of blast-furnace slags are not entirely dependent on indices or calculated modulus using the elementary chemical analysis but rather by potential mineralogical composition established from the chemical composition. 2

The mineralogical compounds from quaternary system CaO-SiO2-Al2O3-MgO that can be found after crystallization from acid and basic blast-furnace slag are:

CS	Pseudo-wollastonite	C3MS2	Merwinite
C3S2	Rankinite	CMS	Monticellite
C2S	Dicalcium silicate	CMS2	Diopside
C2As	Gehlenite	CAS2	Anorthite
C2MS2	Akermanite	Melilite	

Blast-furnace slags entirely crystallized of normal composition do not have hydraulic property or only a very limited one.3 Consequently, most of the experts are in agreement that the slag ought to have a vitreous structure, that is to say the most disorderly one possible in order to obtain a high hydraulicity. Nevertheless, this point of view is not unanimous and for some years there has been expert opinion that crystallization in a vitreous structure can bring a greater reactivity to the slag.4 This opinion was expressed the first time by Budnikov5 who estimated that "vitreous-crystalline" slags have higher potential hydraulic properties than slags vitrified up to 100%. Smolczyk6 thinks that the size and the distribution of crystals in the vitrified blast-

furnace slag have an effect upon hydraulic power. According to Smolczyk, crystallized components ought to be distributed in a homogeneous way in the vitreous phase in the state of submicroscopic nuclei (less than a micrometer).

Demoulian and Gourdin's study<sup>7</sup> which was presented at the 7th International Congress on the Chemistry of Cement has confirmed entirely Budnikov's conclusion that for an identical chemical composition a perfect vitrification is not the criterion of a highest reactivity (see enclosure I). That diagram shows that the ratios of compressive strengths of mortar cubes to the rate of crystallization of slags from the same origin are not linear.

It can be seen that gradients of the curves are positive when the crystallization rate is between 0 and 5% and that beyond 5% the gradients become negative. Nevertheless, strength decreases are not proportional to the increase of crystallization rates.

Different hypotheses have been put forward to explain those results. It has been observed that during the crystallization the first phase crystalline is composed of merwinite  $C_3MS_2$  and that consequently the phase still liquid increases in alumina. If the slag is then quickly cooled, the vitreous phase will have a different chemical composition from the average composition of the entire slag.

Smolczyk<sup>6</sup> has pointed out that the increase of  $Al_2O_3$  rate in a quaternary slag glass gives an improvement of hydraulic properties particularly at the young ages.

At the beginning of the crystallization the vitreous phase diminishes in proportion, but as its reactivity increases there will be observed an increase of hydraulic properties as long as the crystalline phase proportion does not exceed 5%. Beyond this amount hydraulic properties begin to diminish but this reduction is not proportional to the vitreous phase reduction.

When an acid attacks glassy slags containing a crystalline phase, preferential lines of attack are observed by optical microscope. These show microscopic heterogeneousness that can be produced: by nuclei of crystallization, different chemical compositions, and higher internal tensions in the glass.

Studies of the microcrystals influence on slag glasses have been undertaken since the pelletization process has appeared. Compared to the classical granulating process, the pelletization operation is characterized by a lower speed of cooling which produces from the molten slag a material containing a certain proportion of crystalline phase. If pelletized slag were judged only on the vitrification criterion it would be considered as a lower quality product for the concrete industry.

On the contrary, several studies in different countries have proved that pelletized slags can have higher hydraulic powers compared to granulated slag produced from the same

identified origin. The explanation of this superiority is precisely due to the microcrystals that increase the heterogeneousnesses of the structure into the vitreous matter. It must not be forgotten that in the cements containing slag, the mechanical strengths depend not only on the slag by itself but also on the clinker which is associated with it.

In conclusion, a cement containing blast-furnace slag is a complex material from which it is not possible to foresee the strength development from hydraulic index of slag chemical compositions and from the clinker as a setting catalyst, or from the measure of the vitrification rate as this procedure has been practiced in the past. Consequently, an investigation and report by ASTM should be undertaken to document this very important matter. The work that we propose would clarify the cementitious value of granulated slag on one hand and pelletized slag on the other.

#### BIBLIOGRAPHY

1. Bogue, RH, The Chemistry of Portland Cement, 1947, pages 284 and 548.
2. Gourdin, M., Composition Mineralogique Potentielle des Laitiers Vitrifies de Haut Fourneau, Climents, Betons, Platres, Chaux No. 727 - 6/80, pages 363-365.
3. Budnikov, P.O., Pankratov, V.I., Activite Hydraulique de certaines Phase Cristallisees et Vitrifiees du Laitier de Haut Fourneau, Dokaldy Akademi Nauk SSR - 148 No.2 - 1962.
4. Rojak, S.M., Structure et Activite Hydraulique des Laitiers de Haut Fourneau, Cement No.8 - 1978, pages 4 and 5.
5. Bunikov, P.O. - Znacko Javorskij, Laitiers de Haut Fourneau Granules et Cimente au Laitier Gosstrojizdat Moscow, 1953.
6. Smolczyk, H.G., Structure et Caracterisation des Laitiers, 7th International Congress on the Chemistry of Cement - Paris, 1980, Volume I - Rapports principaux - pages III 1/3 to 1/16.
7. Demoulian, E. - Gourdin P. et Autres, Influence de la Composition Chimique et de la Texture des Laitiers sur leur Hydraulicite, 7th International Congress on the Chemistry of Cement - Paris, 1980, Volume II - Communications pages III 89 to III 94.

ENCLOSURE I MICROCRYSTALLIZATION INFLUENCE

