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J. Kaknics¹, V. Montouillout⁵, A. Danezan⁵, S. Blotevogel⁴, L. Doussang², A. Ehrenberg³, D. Hart⁶, H. Bornhöft⁶, M. Cyr⁴, J. Deubener⁶

ACTISLAG - NEW ACTIVATION ROUTES FOR EARLY STRENGTH DEVELOPMENT OF GRANULATED BLAST FURNACE SLAG

¹ *ArcelorMittal Maizieres Research, Voie Romaine, 57283 Maizières-les-Metz, France*

² *Ecocem Materials, 324061, Block F1, Eastpoint Business Park, Dublin 3, Ireland*

³ *Institut Fur Baustoff-Forschung EV, Bliersheimer Str.62, Duisburg 47229, Germany*

⁴ *LMDC, Université de Toulouse, INSA/UPS Génie Civil, 135 Avenue de Rangueil, 31077, Toulouse cedex 04, France*

⁵ *CNRS CEMHTI, 1D ave de la Recherche Scientifique, 45071 Orléans, France*

⁶ *TU Clausthal, Adolphroemer-Strasse 2A, Clausthal-Zellerfeld 38678, Germany*

Ground granulated blast furnace slag (GGBS) containing binders have superior long-term properties but starting from a certain addition level early strengths development is below the ordinary Portland cement (OPC). The RFCS project ActiSlag aims to increase GGBS value via improving short-term reactivity and develop new products containing more than 80 wt.-% of GGBS with at least as good mechanical performance as CEM II class products. Two main topics were addressed so far; (1) the fundamental understanding of the relation between structure, reactivity and performance of industrial slags and (2) modification of the slag chemical and physical properties in liquid state. Several industrial GGBS samples from all over Europe were characterized using both classical methods and high precision tools. Among them, solid-state nuclear magnetic resonance (NMR) spectroscopy revealed the correlation between mechanical performance and structure of the glass network. Differential scanning calorimetry (DSC) performed on hyperquenched slag samples allowed determining the fictive temperature, a characteristic parameter of cooling history. This analysis showed that the cooling rate correlates with particle size and that granulation conditions can impact the slag reactivity. The liquid slag modification trials showed a clear positive effect of alkali and alkaline earth oxide additions as well as of Al₂O₃ addition. The negative effect of TiO₂ was confirmed. The mechanisms behind these effects are being studied doing further NMR analysis and applying synchrotron-based techniques.

1. Introduction

Ground granulated blast furnace slag (GGBS) is a common cement additive in class CEM II and CEM III, replacing clinker/Portland cement up to 80 wt.-% in some niche applications. Although GGBS-containing binders have superior long-term properties, starting from a certain addition level early strengths development is below the Portland cement or cements with lower additions levels [1]. Moreover, pure GGBS reaction with water is slow and therefore slag is typically activated by clinker or other lime-based materials.

GGBS is generated in a two-step process: liquid slag (LS) is evacuated from the blast-furnace through a runner which lead to the granulator, where the LS is drastically cooled down by water. The resulting material has the aspect of a sand and called granulated blast-furnace slag (GBS). GBS is then brought to a grinding facility to reduce the grain size at the level of OPC. This final product is the GGBS

Cement makers have for long been trying to establish compositional ratios able to predict mechanical properties of GGBS in formulations **Erreur ! Source du renvoi introuvable.** The positive impact of slag main constituents such as CaO, MgO or Al₂O₃ on strength development is frequently discussed in literature and numerous reactivity indices, have been proposed, e.g. basicity (CaO+MgO)/SiO₂ [3]. However, these indices work well only in certain cases as different overlapping parameters influence slag reactivity such as chemistry, granulation process, glass content and structure, fineness, activation system etc. Therefore, a simple correlation between chemistry and reactivity does not exist. Furthermore, it is well known that small contents of certain constituents may have a big influence on reactivity (in the case of TiO₂ negative) [6]. Adjustments of blast furnace slag composition to improve its future reactivity performance is thus a potential solution [7].

Generally, a structural organization of highly vitreous GBS grains can be expected at different scales; molecular- ("glass structure" itself, i.e. chemical species, network topology and connectivity but also volatile-speciation and complex/colloid-formation), nano- (amorphous phase and nanocrystal precipitation), meso- (crystals, redox-boundaries) and micro-scale (bubbles, crystals, striae, redox-bands). As only few of the microscopic structures have been studied in the past, such as the crystal fraction

[8][9], the influence of the other structural parameters on the cementitious performance of GGBS is only poorly understood.

In the frame of the RFCS project ActiSlag two industrial partners -ECOCEM, producer and seller of GGBS and ArcelorMittal, producer of LS and GBS- are joint by four research laboratories combining their expertise from different fields; civil engineering (LMDC), glass science (TU Clausthal), independ slag expert at international level (FEhS) and material structural characterization (CNRS-CEMHTI) to reach these objectives. The project started in 2017 and runs over four years. ActiSlag's global objective is to define efficient activation routes based on a two-step process to produce a "second generation GGBS" (Ground Granulated Blast Furnace Slag) which will be assessed in formulations for concrete or dry-mix mortar. The target is to reach 80 wt.-% GGBS addition in cement while keeping the specifications of CEM II (20 wt.-% of classical GGBS). This paper summarizes the main results achieved so far regarding the investigation of relation between structure and performance of industrial blast furnace slag characterization and modification of liquid slag at laboratory scale.

2. Multiscale characterization of selected samples

This study aimed to understand the difference in mechanical properties between slags of different origins. Seven European GBS samples were studied in detail based on different criteria; very low or very high basicity, high Al_2O_3 content, grain porosity, high/low bulk density and different granulation conditions. The link between structure and reactivity was studied regarding both the major oxides (CaO , SiO_2 , MgO , Al_2O_3) and minor oxides (FeO , TiO_2 , MnO , Na_2O , K_2O). The multiscale characterization was conducted using X-ray diffraction (XRD), solid state nuclear magnetic resonance spectroscopy (NMR), scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) and transmission electron microscopy (TEM). Both SEM and TEM investigations showed a homogeneous glass phase with no phase separation or demixing. EDS analysis showed a homogeneous composition regarding the main elements with a local dispersion without pattern of some minor elements (Ti, Na, K, Fe, Mn) at a nanometric scale.

Description of the glass network

The glass structure was investigated by studying the environment of Si and Al atoms by NMR spectroscopy. The ^{29}Si MAS NMR spectra of all samples were recorded on a Bruker AVANCE 400MHz spectrometer ($B_0=9.4\text{T}$, $\nu_{\text{rf}}(^{29}\text{Si})=79.4\text{MHz}$, $\nu_{\text{rot}}=10\text{kHz}$). The spectra obtained are presented in Figure 1a **Erreur ! Source du renvoi introuvable.**, in order of decreasing mechanical performance from top to bottom. The spectra all display a single broad signal, centred at around -75 ppm and spreading out from -65 ppm to -90 ppm. The GBS13 spectra is wider than the others, spreading out from -65 ppm to -115 ppm due to paramagnetic influence. The broadening of the ^{29}Si NMR signal results in the overlapping of numerous contributions corresponding to the different silicon environments; SiO_4 tetrahedrons can appear as Q^0 to Q^4 units [10] charge compensated by different modifier cations (Ca^{2+} , Mg^{2+} , Na^+ , K^+), and connected (or not) to other network formers such as Al^{3+} , Fe^{3+} , Ti^{4+} . The chemical shift distribution of the ^{29}Si NMR signal can give an estimation of the polymerization degree of the glass network, with the position of the signal giving information about the average silicon environment in the sample and the full width at half maximum (FWHM) information about the variety of the Si environment. A sample with a higher chemical shift will be less polymerized than a sample with a lower chemical shift and similar width, and at similar positions, a sample displaying a broader signal will contain a larger variety of silicon environments than a sample displaying a thinner signal. The position in ppm and FWHM of each signal were determined using the DMFit software [11]. The samples studied appear to have a depolymerized network composed mainly of $\text{Q}^1_{(0\text{Al})}$, $\text{Q}^2_{(0\text{Al})}$ and $\text{Q}^2_{(1\text{Al})}$. The number of NBO per tetrahedra based on charge balance can be simply estimated, using a modified NBO/T formula (1) considering only the tetrahedrons of the Si atoms. The NBO/T formula gives information about the polymerization degree of the glass network. The slag components can be divided into network former (SiO_2), network modifier (CaO , MgO , MnO , FeO , Na_2O and K_2O) and into the intermediate oxide Al_2O_3 .

$$\frac{\text{NBO}}{T_{\text{Si}}} = \frac{2(\text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} - \text{Al}_2\text{O}_3)}{\text{SiO}_2} \quad (1)$$

Network formers will break the Si-O-Si bonds and therefore lead to the depolymerization of the glass network. The higher the NBO/T formula, the more

depolymerized the glass structure is. The ^{29}Si chemical shifts obtained by NMR and the calculated $\text{NBO}/\text{T}_{\text{Si}}$ values were plotted in Figure 2. A quite good correlation between the calculations and the measured values can be observed. The analyses of the Al environment gave similar results to all GGBS samples. All the spectra obtained are very similar, with a main signal centred at around 65ppm and a smaller shoulder at 35 ppm (Figure 1b). The main signal is associated with the presence of Al in four-fold coordination and the smaller shoulder is consistent with five-fold coordinated Al. The small differences in the shift of the main peak of GBS samples indicates a difference of four-fold coordinated environment. This difference could in fact be the presence of NBOs on Al tetrahedrons.

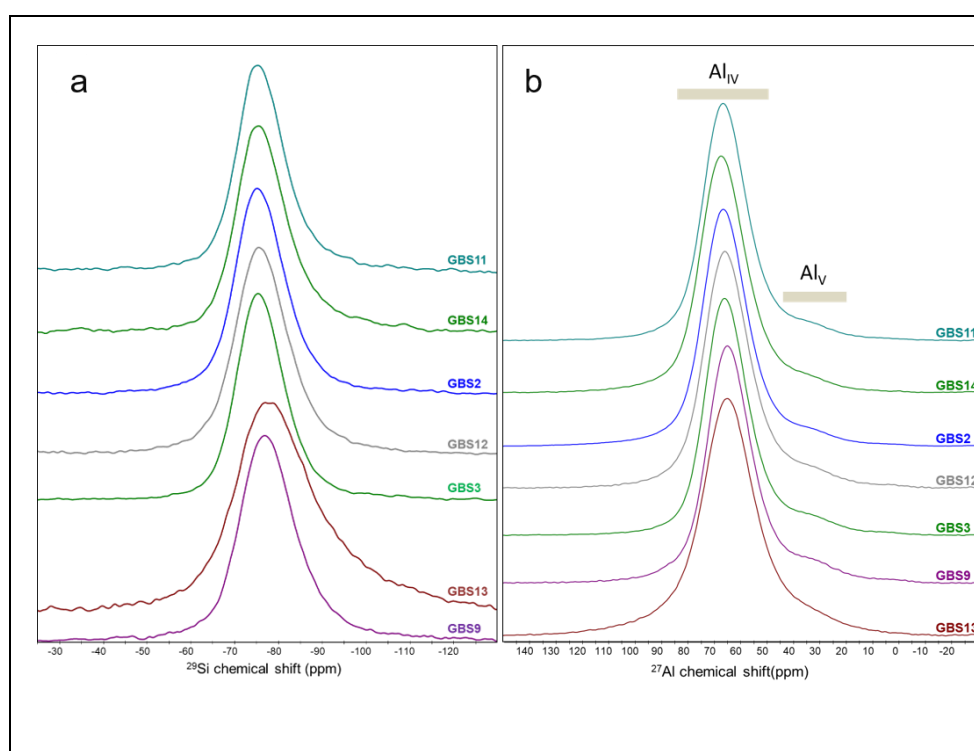


Figure 1 –(a) ^{29}Si MAS spectra and (b) ^{27}Al MAS spectra of all GBS samples

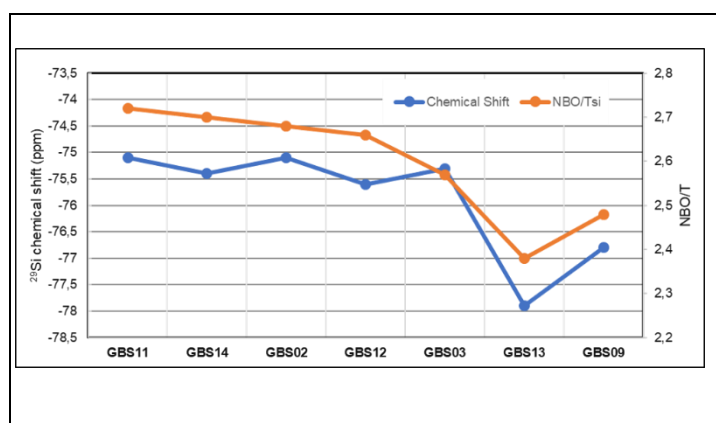


Figure 2- ^{29}Si chemical shift and $\text{NBO}/\text{T}_{\text{Si}}$ evolution according to the performance of the samples

Thermal history of GBS

The glass transition temperature (T_g) and the fictive temperature (T_f) of samples was determined by differential scanning calorimeter (DSC) measurements at TU Clausthal. The original GBS was sieved into a finer (355 - 500 μm) and a coarser fraction (> 2 mm) to investigate the influence of particle size. The glass transition temperatures of the selected slags range from 724–743 $^{\circ}\text{C}$. This is up to 200 $^{\circ}\text{C}$ above the glass transition temperature of the soda lime silicate standard glass. The rather narrow range of GBS T_g values leads to the assumption that the glass structure of the slags in relaxed state should be very similar. Hence, it is not possible to predict the reactivity of GBS being used as an additive in cement by this method.

The fictive temperature contains information about the cooling history of glasses and it is defined as the temperature at which the liquid structure of a glass melt is frozen in. For the calculation of T_f , a specific heat measurement was performed with a sapphire standard as reference followed by using the area-matching method [12][13]. The calculated fictive temperatures of the small and large fractions of the selected slags are listed in Table 1. As can be seen, the fictive temperatures of small fractions (355 - 500 μm) vary from 803 to 838 $^{\circ}\text{C}$ and of the large fraction (> 2 mm) from 780 to 820 $^{\circ}\text{C}$. The differences in T_f can be explained by the fact that the selected slags were produced at several granulation facilities under different cooling conditions. Furthermore, it is remarkable that the small fractions always show a higher fictive temperature than the large fraction of the same GBS sample. Therefore, it can be concluded that smaller particles undergo a more efficient cooling during the granulation process than bigger particles. Mortar tests performed by FEhS on the two different fractions showed a clear positive effect of the faster cooling rate on strength development.

	GBS9	GBS13	GBS3	GBS12	GBS2	GBS14	GBS11
Tf / $^{\circ}\text{C}$ Small fraction	824	803	837	820	836	838	817
Tf / $^{\circ}\text{C}$ Large fraction	790	785	820	787	817	787	780

Table 1- Fictive temperature of small and large fractions of industrial GBS samples

3. Upstream modifications

The aim of this study was to test chemical modifications of liquid slag to enhance its hydraulic reactivity. The trials were divided into two sets: investigating the effect of major components (CaO, MgO, Al₂O₃, TiO₂ and SiO₂) on GGBS reactivity via a Taguchi experimental design and screening the effect of minor elements (P, K, V, Cr, Mn, Sr, Zr, Sn, Cs, Ba, Ce) usually not present or only in a very small quantity in the slag. A lab-scale melting and granulation protocol was developed at ArcelorMittal allowing preparing a large number of samples in small quantities (200 g) and achieving a microstructure similar to industrial slag. Industrial GBS samples were mixed with additions and placed in a graphite crucible in a preheated furnace. The samples were quenched in a laboratory scale granulator. The granulated slag was dried overnight then ground to a Blaine fineness of 4100 cm²/g. The reactivity of modifications was quantified using the R3 calorimetric tests in a TAM Air isothermal calorimeter.

Modification of major components

The Taguchi experimental design was composed of four factors (Al₂O₃, CaO, MgO and TiO₂) at four levels. SiO₂ was not selected as a factor, its role consisted in completing the composition to 100 wt.-%. To control the dilution of minor components, the same amount of slag and the same amount of total addition was used for each sample. Lab grade Al₂O₃, CaO, MgO, TiO₂ and SiO₂ (Fontainebleau sand) were mixed to the slag prior to the fusion to obtain the desired composition. The effect of each factor was calculated by taking the mean of samples with the same concentration level (the particularity of the Taguchi array is that it is strictly orthogonal) and deducing the mean of all modifications. The calculated effect of Al₂O₃, CaO, MgO and TiO₂ are presented in [Figure 3](#). As Si was not entered as parameter, its effect cannot be computed by this model. This experimental matrix does not consider the possible interactions between the elements; further modification trials are necessary to have a full picture of the effect of these elements. In the cases of compositions with very high basicity (>1.4 CaO/SiO₂), it is not possible to obtain completely glassy material and therefore the presence of crystalline fraction can influence the values of the calorimetric measurements. On the other hand, it was interesting to see that crystalline phases do not necessarily have a negative influence on the reactivity. Indeed, up to a certain level merwinite can activate the slag hydration [14].

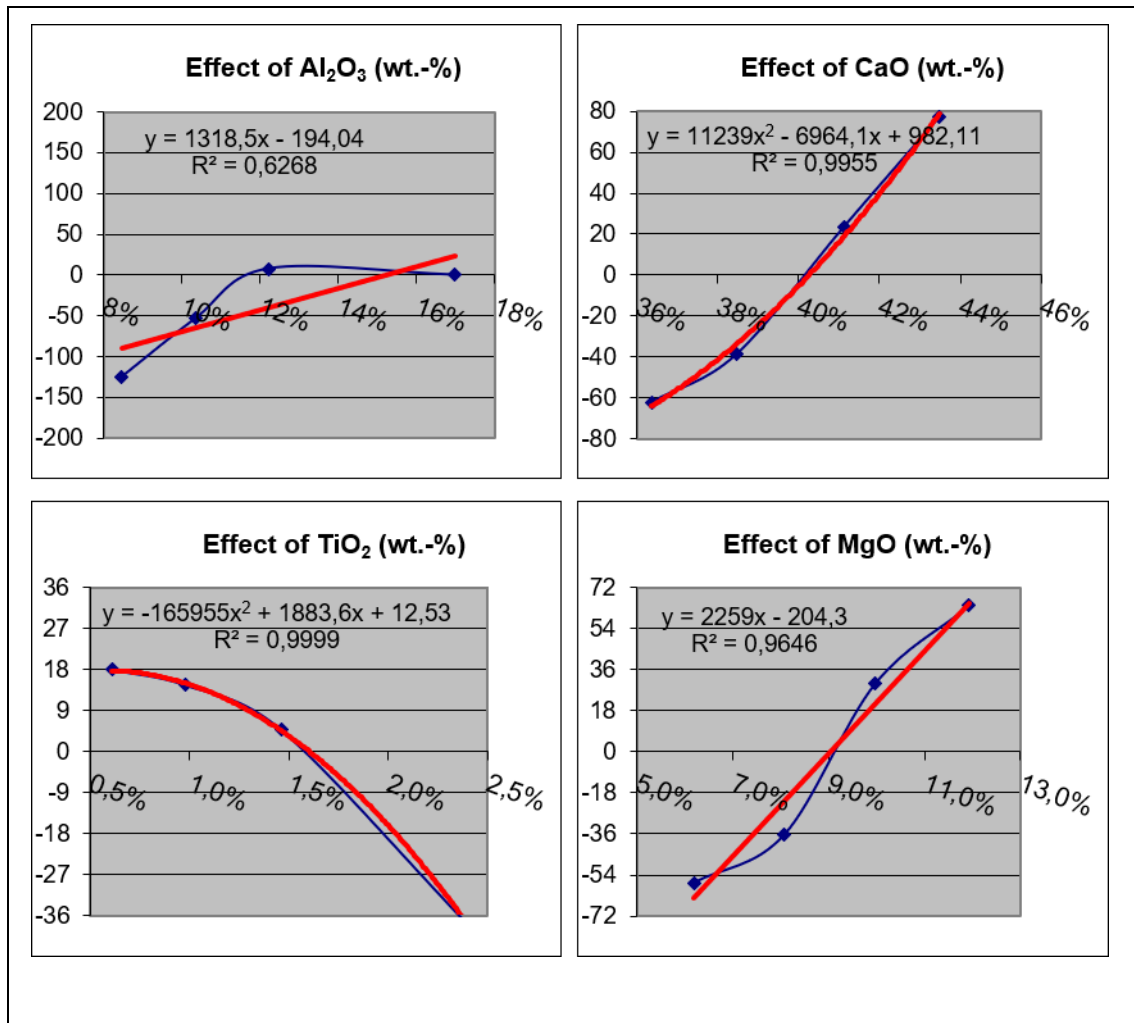


Figure 3 – Effect of modification of major components

Screening of minor element

The following components were tested in few weight percentages: CsCO₃, K₂O-SiO₂, K₂CO₃, BaO, CeO₂; SrO₂, MnO₂, MnO, Cr₂O₃, SnO₂, ZrO₂, V₂O₅, Ca₃(PO₄)₂. Based on the NBO/T theory, we expect that elements with 1+ and 2+ valency will depolymerize the glass structure hence they will increase the slag reactivity; while 4+ and 5+ ions will be rather network formers. The question here was if their integration in the glassy network will have a destabilizing effect. The role of 3+ elements depends on the environment, they can be both network former or modifier. The SEM-EDS analysis of the modified samples showed that some addition did not combine with the glass structure but formed metallic phases with the remaining iron content of the slag. Indeed, it is well-known in metallurgy that some elements such as Mn, P, Cr, Cu and Ni have rather affinity to the metallic iron than to the oxides. Despite the very low amount of Fe (<1 wt.-%), the experimental condition (graphite crucible and reducing atmosphere) was enough to prevent combination with the glassy GBS. Figure 4

presents the heat development of the modified samples with the unmodified industrial GBS as baseline. ZrO_2 has a significant negative effect, probably via reinforcing the glass network, while Cr_2O_3 , V_2O_5 , SnO_2 and CeO_2 only slightly decreased reactivity. As expected, alkali and alkaline earth metals have significant positive effect on the reactivity, which we attribute to their depolymerizing effect.

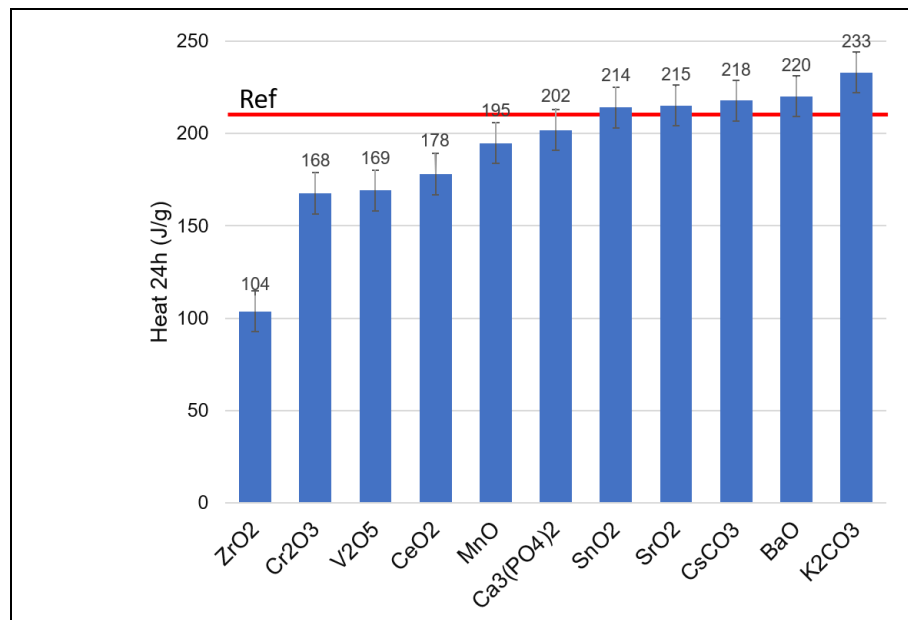


Figure 4 – Heat of hydration development of modified GBS samples

4. Conclusion

In this study, seven industrial GBS samples were investigated in detail. NMR investigations outlined a correlation between the chemical shifts obtained by NMR and the calculated NBO/T_{Si} values. The determination of fictive temperatures of two different size fractions of the selected GBS samples showed that the small fraction always shows a higher fictive temperature than the large fraction. That allows the conclusion that a difference in cooling rates exists during the water-jet granulation at which the smaller grains have higher cooling rates. Mortar tests performed on the different fractions showed a positive effect on reactivity of faster cooling rate. Chemical modifications of major elements confirmed the positive effect of Al_2O_3 , CaO and MgO on slag reactivity. The negative effect of TiO_2 was confirmed. The interaction between these elements are not described for the moment, additional trials will be performed to construct a numerical model allowing predicting slag behavior based on compositional changes. Testing new elements revealed that some additions such as Mn, Sn, P form alloys with the residual Fe in the slag and do not interact with the glass structure of the

slag itself. Other network forming elements as Zr, can significantly decrease GGBS reactivity even at low concentrations. The highest increase in reactivity was achieved with the addition of potassium oxides. Potassium probably decreases the polymerization degree of the glass, thus enhance its early strength development. Further investigations on the hydration mechanisms of the modified samples will be carried out to be able to describe the role of these additions in slag reactivity.

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