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Assessing chemical reactivity of blast furnace slag as supplementary cementitious material

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Abstract

Reduction of CO_2 emissions associated with cement production represents one of the most important and urgent challenges for the cement industry. Thus, the replacement of cement by Supplementary Cementitious Materials (SCM) has been a widely adopted industrial practice. The reactivity of slag is considered to be an important parameter for assessing its suitability as a cement replacing material in concrete. The aim of this paper is to determinate reactivity of slag originating from various sources using isothermal calorimetry and bound water measurement.

Key words: blast furnace slag, supplementary cementitious material, isothermal calorimetry, bound water

Procjena kemijske reaktivnosti zgure visoke peći kao dopunskog cementnog materijala

Sažetak

Smanjenje emisije CO_2 povezano s proizvodnjom cementa predstavlja jedan od najvažnijih i najhitnijih izazova za cementnu industriju. Stoga je zamjena cementa mineralnim dodatcima široko prihvaćena industrijska praksa. Reaktivnost zgure smatra se važnim parametrom za procjenu njezine prikladnosti kao mineralnog dodatka za cement u betonu. Cilj ovog rada je utvrditi reaktivnost zgure različitog podrijetla koristeći izotermalnu kalorimetriju i određivanje sadržaja vezane vode.

Ključne riječi: zgura visokih peći, zamjenski cementni materijal, izotermalna kalorimetrija, vezana voda

1 Introduction

Carbon dioxide emissions are the main driver of global climate change. It is now known that the world must reduce emissions to avoid the worst effects of climate change. Emissions growth has slowed over the last few years, but they have yet to reach their peak [1]. Although cement is a low-cost and low-energy product compared to other construction materials, it is responsible for 6 – 8 % of anthropogenic CO_2 emissions due to its extremely large-scale production. Reduction of CO_2 emissions associated with cement production is thus one of the most important and urgent challenges facing cement industry. Cement industry is undoubtedly facing an increasing demand for supplementary cementitious materials (SCMs) as an alternative to cement and, in this context, the global and local availability of the materials should also be considered as an important parameter [2].

As separate materials and in contact with water, most SCMs do not show significant hydraulic reactions of cementitious value. However, as fine powders and under alkaline aqueous conditions, or in contact with calcium hydroxide, they will react chemically through the „pozzolanic reaction“ [2]. Nowadays, the replacement of cement with SCMs is a widespread industrial practice. Moreover, the development and characterization of SCMs has attracted considerable attention in the academia and research circles for at least the last 20 years [3-7].

SCMs affect the hydration kinetics of clinker phases and of the formed products. In general, the reaction of SCMs is slower than that of the main clinker phase in Portland cement. SCMs affect hydration of blended or composite cements in two main ways. First, through physical effects that also occur in inert fine powders or fillers, hence the collective term "filler effect" [8-9]. Secondly, by participating in chemical reactions to form hydration products. This chemical reaction follows the dissolution-precipitation mechanism, where three main components are the solid reactants, the solid hydrate reaction products, and the (pore) solution.

Two main types of chemical behaviour are distinguished for the SCM as a solid reactant. If the reaction of the SCMs consumes $Ca(OH)_2$, it is called a "pozzolanic reaction". If the reaction does not require $Ca(OH)_2$ or if it is used mainly for pH activation, then it is called a "hydraulic" or "latent hydraulic reaction". The fineness of SCMs affects the reaction kinetics of SCM particles as their dissolution increases with an increase in surface area. Moreover, the number of nucleation sites for hydrate precipitation and growth increases with a decrease in SCM particle size, which can accelerate the hydration process for both SCMs and clinker phases at early ages [2]. In addition, the presence of SCMs in blended cements increases the early hydration of the cement phases by the filler effect, which provides additional water and space for the formation of hydration products due to of the effectively lower water- clinker ratio [2].

1.1 Ground granulated blast furnace slag

Ground granulated blast furnace slag (GGBFS), a by-product of the steel manufacturing industry, is used as an effective partial cement replacement material and has already been shown to improve various properties of concrete. It was found that the reactivity as well as chemical composition of GGBFS depends on the properties of GGBFS, which in turn depend on the source of GGBFS, the type of raw material used, the process and the cooling rate [10-11]. GGBFS originating from the same blast furnace has a fairly constant composition, as consistent quality of pig iron is a priority for blast furnace operations [11]. Blast furnace slag is formed by the combination of earthy constituents of iron ore with limestone flux. When the molten slag is quickly quenched with water in a pond, or cooled with powerful jets of water, it forms a fine, granular, almost completely non-crystalline, glassy form known as granulated slag, which has latent hydraulic properties [10]. The latent hydraulic reactivity of GGBFS was discovered in the 19th century by Emil Langen. Due to its latent hydraulic properties, GGBFS begins to hydrate when it comes into contact with water. However, this reaction decreases with time. The GGBFS hydration continues only in the presence of an activator. The activation potential depends largely on GGBFS properties [11]. Basically, major chemical constituents of blast furnace slag are CaO, MgO, SiO_2 and Al_2O_3. Its crystalline phases are mainly of the melilite solid solution series, β-C_2S and amorphous phase. Most of the minerals are non-hydraulic, except for small amounts of β-C_2S [12]. In general, the reactivity of the GGBFS increases with an increase in CaO, Na_2O, and Al_2O_3 content, and with a decrease in SiO_2, FeO, TiO_2, MnO, and MnS content [11] . One of the classical methods to increase slag reactivity is to increase fineness of the slag [13].

1.2 Assessment of slag reactivity

The reactivity of slag is considered to be an important parameter for assessing its suitability as a cement replacement material in concrete [14]. To better understand the factors affecting the reaction rate of SCMs, it is important to have a good method to evaluate the degree of reaction of these materials independently of the degree of reaction of the clinker component [15]. In this paper, the reactivity of GGBFS was measured using isothermal calorimetry and bound water measurement [16-18]. These methods were developed and proposed by the RILEM TC-267 committee as standard test methods for measuring chemical reactivity of supplementary cementitious materials [17]. Both methods are used to evaluate chemical reactivity of an SCM as determined by cumulative heat release or bound water content measurement of hydrated pastes consisting of the SCM, calcium hydroxide, calcium carbonate, potassium sulphate, and potassium hydroxide cured at 40 °C for 3 and 7 days. Results of these test methods can be used to estimate potential contribution of an SCM to the development of strength, or other properties such as lower permeability, when used with Portland cement. It is important to note no distinction is made in these two test methods between hydraulic and pozzolanic reactivity.

The basic principle of the R^3 test methods is to use a simplified model system to measure response of an SCM separately. This is done to avoid interference and overlap with the clinker hydration reactions that occur in a blended cement system. In addition, the use of laboratory chemicals instead of local Portland cements avoids many variations in the composition of the material. Isothermal calorimetry is a common method for testing cementitious materials. It is used to quantify both the very early reactions (first hour or hours), the onset of the main reaction, and the main hydration peak. The development of most of the properties of cement-based materials is related to their heat release [19].

2 Materials and methods

The main objective of this paper is to determine the reactivity of slags of various fineness as well as the reactivity of slags of various origin. Six distinct types of slags were analysed: GGBFS 1, GGBFS 2, GGBFS 3, GGBFS 4, GGBFS 5. The main constituents of all these slags are SiO_2 (35.40 % – 39.80 %), CaO (34.70 % - 42.50 %) and Al_2O_3 (10.80 % - 13.50 %). For the reactivity study of slag of the same origin, the duration of milling was different for the samples. For the reactivity study of the slags of different origin, the particle size distribution is relatively similar, with d_{50} ranging from 26 to 53 µm.

The reactivity of the materials was studied using a calorimetry test developed under the RILEM TC-267 committee and referred to as the R^3 test [16-18]. Samples of the pastes containing SCM, sulphate, and alkali additive were placed in an isothermal calorimeter TAM Air with 8 channels at a temperature of 40 °C for 3 and 7 days to obtain the total heat release. For each mix, a ratio of $Ca(OH)_2$/SCM and $CaCO_3$/SCM of 3 and 1/2, respectively, was used, while the alkali solution was prepared with 3M of K in the form of KOH and K_2SO_4. All materials and reagents were weighed, mixed and stored at 40 °C in the oven for 24 h before the experiment. A high shear mixer was operated at 1600 ± 50 rpm for 2 min to obtain a homogeneous paste, which was immediately poured into a glass vial and placed in an isothermal calorimeter.

Samples of the pastes for bound water measurement were prepared in the same manner as for isothermal calorimetry. The prepared pastes were placed in a plastic container and then cured in the oven at 40 °C ± 2 °C for 7 days. The pastes were then milled in a mortar and dried at 350 °C for 2 hours. The bound water was calculated by measuring mass change before and after heating at 350 °C. The evaluated chemically bound water of the hydration pastes is used as a measure of the hydraulic reactivity of the SCM.

3 Results

To determine whether the R^3 test is suitable for detecting different reactivity of slags of the same origin but of different milling time (different fineness), the GGBFS 5 slag with different particle size was analysed by isothermal calorimetry and by measurement of bound water. The results are shown in Figure 1 and Table 1. Slags are named GGBFS 5A (time of milling 30 s), GGBFS 5B (time of milling 90 s) and GGBFS 5C (time of milling 180 s) where fineness increases from A to C.

The results of the R^3 test, shown in Figure 1 and Table 1, reveal that the reactivity of GGBFS 5 increases with an increase in milling time. GGBFS 5A has the coarser particle size and the lowest reactivity. On the other hand, the GGBFS 5C slag with the finest particle size has the highest reactivity. The heat release after 3 days ranged from 105.6 Jg^{-1} (GGBFS 5A) to 202.8 Jg^{-1} (GGBFS 5C) and the bound water content ranged from 4.5 % to 6.3 %. The heat release value and the bound water content increase with an increase in fineness of GGBFS 5 slag. Both isothermal calorimetry and the bound water method can detect differences in the reactivity of slag from the same origin with the change in fineness.

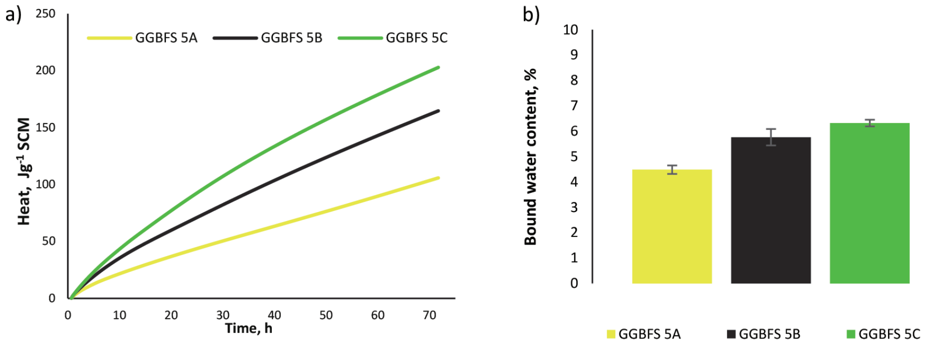

Figure 1. R3 test of GGBFS 5 slag with different fineness values a) heat of hydration; b) bound water content

Table 1. Heat release for GGBFS 5 slag with various fineness values after 24 and 72 hours and bound water content after 7 days

Slag	Time of milling, [s]	Heat release 24 h, [Jg^{-1} SCM]	Heat release 3 d, [Jg^{-1} SCM]	Bound water, [%]
GGBFS 5A	30	42.4	105.8	4.5
GGBFS 5B	90	68.8	164.7	5.8
GGBFS 5C	180	89.5	202.8	6.3

In addition, the R^3 test was performed to determine reactivity of laboratory milled slags of similar particle size distribution (PSD) but of different origin GGBFS 1, GGBFS 2, GGBFS 3, GGBFS 4 and GGBFS 5. Quartz was used as an inert material due to its ability to distinguish the so-called filler effect from the contribution of a reactive mineral addition (GGBFS), [20]. The results are shown in Figure 2, Figure 3, Table 2, and Table 3.

Table 2. Ranking of slags based on heat release (isothermal calorimetry)

Rank	Slag	Particle size d_{50}, [mm]	Heat [Jg^{-1} SCM]			
			6 h	24 h	3 d	7 d
1	GGBFS 1	41	99.8	241.8	358.3	382.0
2	GGBFS 2	36	66.9	197.4	316.6	349.5
3	GGBFS 3	53	36.6	129.4	255.3	312.1
4	GGBFS 4	26	29.1	117.2	220.1	268.2
5	GGBFS 5	31	21.2	77.6	157.1	207.5

According to Figure 2 and Figure 3, all tested slags show significantly higher reactivity than the reference quartz. The release of heat from tested slags after 7 days ranges from 207.5 Jg^{-1} (for GGBFS 5) to 382.0 Jg^{-1} (for GGBFS 1). Compared to other slags, GGBFS 1 slag shows the best results in initial reaction, besides the higher amount of heat released over the 7 days. According to heat release, GGBFS 1 is followed by GGBFS 2 and then by GGBFS 3 and GGBS 4, while the slag with the lowest heat release is GGBFS 5. The results of the bound water test (Figure 3) show almost the same trend in reactivity as the results of the isothermal calorimetry test. The bound water content for the tested slags ranges from 4.7 % (for GGBFS 5) to 7.3 % (for GGBFS 1). Based on the bound water results, the most reactive slag is GGBFS 1, which is followed by GGBFS 2, GGBFS 4 and GGBFS 3, while the least reactive slag is GGBFS 5.

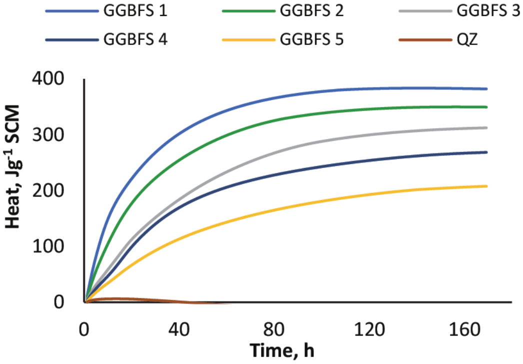

Figure 2. Heat release for slags from different origin, GGBFS 1, GGBFS 2, GGBFS 3, GGBFS 4, GGBFS 5 and quartz (QZ) as reference

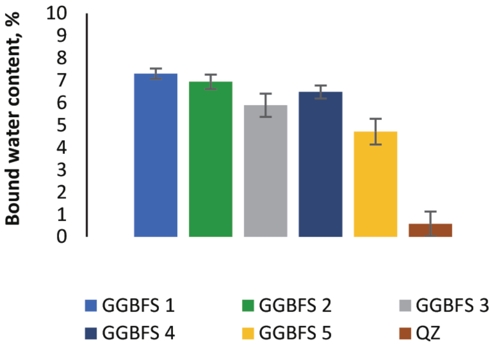

Figure 3. **Bound water content for slags from different origin, GGBFS 1, GGBFS 2, GGBFS 3, GGBFS 4, GGBFS 5 and quartz (QZ) as inert material**

Table 3. Ranking of slags based on bound water content

Rank	Slag	Bound water content [%]
1	GGBFS 1	7.3
2	GGBFS 2	6.9
3	GGBFS 4	6.5
4	GGBFS 3	5.9
5	GGBFS 5	4.7

4 Conclusion and future perspectives

The main objective of the present study was to evaluate reactivity of various available slag types with similar particle size distribution. In addition, the applicability of isothermal calorimetry and bound water measurement for the reactivity of ground granulated blast furnace slag was evaluated. It was found that differences in the reactivity of the slags can be detected using the R^3 protocol for isothermal calorimetry and the bound water test method. The difference in reactivity can be found both for similar slags with different fineness and for the slags of different origin. When there is a significant difference in particle size distribution, then higher fineness of slag results in higher reactivity. However, if the particle size distribution is similar, the reactivity is influenced mainly by the slag chemistry.

These results point to the possibility of using isothermal calorimetry and bound water measurement for slag reactivity prediction. Future research will involve the analysis of slag reactivity with calcium aluminate cement based on isothermal calorimetry, as well as the assessment of phases that are forming through the TGA and XRD analysis. The objective will be to determine which properties of slags are responsible for lower or higher reactivity in the calcium aluminate cement environment.

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