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Mechano-chemical modification of cement with high volumes of blast furnace slag

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Abstract

The application of chemical admixtures significantly improves the performance of cement-based materials. Some admixtures can also be used to modify the cement grinding process and induce changes in the structure of cement minerals due to mechano-chemical activation. A reactive silica-based complex admixture was developed for the modification of cement grinding. This paper examines the effect of grinding on the strength of a modified cement containing granulated blast furnace slag in high volumes. According to the test results, mortars based on the modified cement possess a compressive strength of up to 91.7 MPa, a 62% increase over the reference.

Keywords: Chemical admixtures; Reactive silica, Cement; Grinding; Mechano-chemical activation; Strength; Durability; Granulated blast furnace slag; High-performance cement

1. Introduction

The application of advanced cements with high strength and superior durability is an attractive method of controlling concrete properties and the design of high-performance concrete (HPC) [1–8]. These cements are often based on special clinkers or blended cements: for example, shrinkage compensating or expansive cements, high-early strength cements, and regulated-set cements [1,2]. Among these advanced cements are the newly developed Ultimax cement, blended Pyrament, energetically modified cement, and silica fume cements [5–11].

A novel approach to improving cement performance includes the application of chemical admixtures (or modifiers) at the stage of cement grinding [3]. Using this technique, a number of cement products have been developed. Well known examples include air-entraining, hydrophobic, and plasticized cements; and, also, the family of cements manufactured with grinding aids. It has been suggested that the action of these modifiers is governed by mechano-chemical activation [1,3–8]. Generally, the theory of mechano-chemical activation (MCHA) has been applied to processing nanopowders, pigments, fillers, binders, ceramic, and ferromagnetic materials [12–19].

Mechano-chemical activation is used to describe the chemical conversions in solids induced by a mechanical process such as milling or grinding [14,15]. The mechanical processing usually results in the formation of dislocations and other defects in the structure of the material [15]. In the case of MCHA, the mechanical impacts cause the development of elastic, plastic, and shear deformations leading to fracture, amorphization, and even chemical reactions in the solid state. Characteristic features of MCHA are summarized in Fig. 1. Ball

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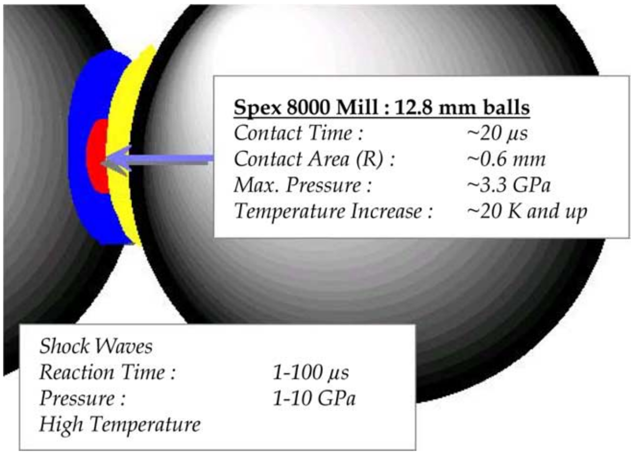

Fig. 1. The mechanism of mechanically induced solid state reactions. (*Courtesy of V. Balema, Iowa State University of Science and Technology, reproduced with permission from* [15].)

milling breaks down the crystallinity of solid reactants and provides a transfer of mass required for chemical reactions. In addition, high pressure and shear stress facilitate both the phase transitions and the chemical transformations of solids. The energy in the form of various lattice defects, accumulated by the solid during the mechanical processing, can support or even trigger various chemical transformations [15].

Based on this theory, a significant improvement of cement strength has also been reported [1,3–8]. For example, low water demand binder (LWDB) is produced by intergrinding cement and a dry modifier at a high energy [8]. In spite of a similar process, previously described [1,10], only the application of a specially selected admixture (modifier) at a relatively high dosage (about 4%) resulted in a cement with both reduced water demand and high strength.

Complex admixtures for application in cement technology have been developed [7]. Generally, these admixtures contain a reactive silica-based sorbent, an effective surfactant, and some minor corrective components [3,7]. Supersilica, a reactive silica-based complex admixture (RSA), was produced using this principle. Although all the effects of RSA have not been completely investigated, it is hypothesized that, when added during the cement grinding process, RSA modifies the surface of cement particles and also promotes the formation of highly reactive phases [3]. Scanning electron microscopy (SEM) helps to reveal some details of interaction between RSA and cement, such as nano-indentations on the surface of cement particles (Fig. 2). Further, silica component of RSA also acts as a micro-filler and participates in a pozzolanic reaction. The mechano-chemical activation of cement with RSA results in a new product, high-performance (HP) cement.

High-performance cement can be defined as a material manufactured by the mechano-chemical activation

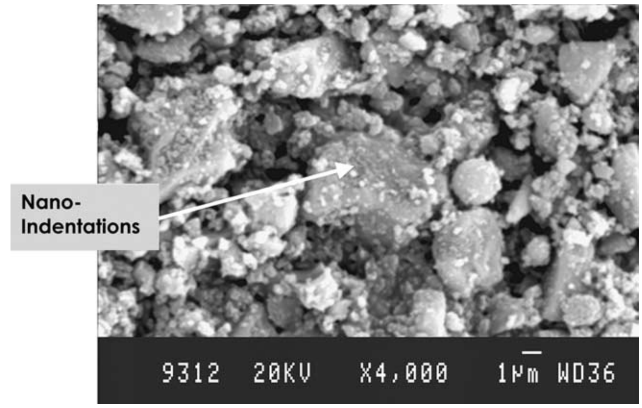

Fig. 2. Scanning electron micro-photograph of HP cement.

of certain proportions of clinker, gypsum, a complex admixture (RSA) and, optionally, a mineral additive of industrial (IBPW) or natural origin [3]. The application of HP cement imparts high strength and extreme durability to the concrete or mortar [3]; and its high strength can be used for engineering of a cement with a high volume of mineral additives (HVMA) [20,21]. In this case, relatively large amounts (up to 70%) of portland cement clinker can be replaced by inexpensive, locally available mineral additives. Natural pozzolanic materials, sand, limestone, granulated blast furnace slag, fly ash, glass cullet and ceramic waste, all can be used as mineral additives in HVMA cements [20].

2. Research significance

The effect of silica fume (SF) on the behavior of cement-based materials has been extensively reported in the literature [2]. A number of reports on SF cement evaluate its positive effect on cement grinding and the consequent improvement of the final product [4–6]. Less information is available on the behavior of RSA at the grinding stage. It was expected that SF and RSA would improve the properties of HVMA cements containing granulated blast furnace slag. The evaluation of the effect of SF, RSA, and the parameters of the mechano-chemical activation on the cement properties is important for a better understanding of the processes involved in MCHA and, therefore, for the development and production of high-performance cement-based materials.

3. Experimental program

3.1. Materials used

The reference cement was portland cement CEM-I 42.5 [22] (NPC, Type I according to ASTM C150

[23]). Three additional components were used in the research: ground granulated blast furnace slag (GGBFS), silica fume (SF), and a reactive silica-based complex admixture (RSA). The chemical composition of the main cementitious materials is presented in Table 1. Ground granulated blast furnace slag was an intermediate product used for the manufacturing of portland-blast furnace slag cement; it had a Blaine specific surface area of 358 m^2/kg (compared with NPC having a Blaine area of 312 m^2/kg). Standard RILEM Cembereau sand [24] and regular tap water were used for the preparation of the mortars.

3.2. Mixture proportioning

The strength properties of seven different cements were investigated. These included SF and HP cements produced with three durations of intergrinding (10, 20, or 30 min) and the reference cement. The SF and RSA were used at the same dosage of 10% (by weight). The constant amount of GGBFS (45%) was used in all cements (except the reference). The composition of the investigated cements is given in Table 2. The mortars were proportioned following the recommendations [3], with *W/C* adjusted to provide a constant flow and a sand-to-cement ratio (*S/C*) of 2.75 (similar to the requirements of ASTM C109 [25]). This approach proved to be critical for the evaluation of high strength binders [3,8].

3.3. Preparation of specimens

Samples of SF and HP cement were obtained by intergrinding the specified mixtures in a laboratory ball mill. The sample weight was 5 kg and the grinding media weight was 65 kg. Grinding times were 10, 20, or 30 min. The resulting fineness data of the investigated cements are summarized in Table 2 and Fig. 3. Mortars based on the cements obtained were prepared following the procedure of EN 196-1 [26]. The flow table was applied to obtain the standard flow of 105–115 mm as per ASTM C109 [25]. Using a jolting table for the mortars, test specimens were cast into three-gang prism molds (40 × 40 × 160 mm) in accordance with EN 196-1 [26]. After the compaction procedure, the molds were placed in a humidity cabinet for 24 h (keeping a relative humidity of 95% and a temperature of 20 °C). Following this period, the specimens were removed from the molds and kept in 20 °C water until the time of test.

3.4. Tests performed

The experimental program investigated the effect of mineral additives and the duration of MCHA on:

- fineness of cements;
- normal consistency and setting time;
- compressive strength.

The particle size distribution of investigated cements was measured by a SILAB laser diffraction analyzer. Normal consistency and setting time were determined following the procedure of EN 196-3 [27]. Compressive strength tests were conducted using the portions of prisms broken in flexure as per EN 196-1 [26]. The compressive strength results are the average of the four test values. The mortars were tested at the ages of 2, 7, and 28 days.

Table 1
Chemical analysis of cementitious materials

Chemical composition	Portland cement	Granulated blast furnace slag	Silica fume
SiO_2	19.4	37.4	90.0
Al_2O_3	4.8	10.9	0.4
Fe_2O_3	3.6	0.6	0.4
CaO	63.7	35.9	1.6
MgO	1.9	8.1	1.0
SO_3	2.7	2.1	0.4
Na_2O	0.2	0.4	0.5
K_2O	0.8	1.2	2.3
Loss of ignition	2.4	–	3.0

Table 2
Composition and fineness of investigated cements

Cement type[a]	Cement composition				Duration of MCHA (min)	Fineness	
	NPC	GGBFS	SF	RSA		Median size (μm)	Blaine (m^2/kg)
NPC	100	–	–	–	–	15.4	312
SFC-10	45	45	10	–	10	13.0	689
SFC-20	45	45	10	–	20	11.4	710
SFC-30	45	45	10	–	30	10.8	748
HPC-10	45	45	–	10	10	12.5	639
HPC-20	45	45	–	10	20	10.2	679
HPC-30	45	45	–	10	30	8.4	726

[a] NPC—reference portland cement; SFC—# SF cement; HPC—# HP cement; the additional number after the main notation identifies the duration of intergrinding (as 10, 20, or 30 min).

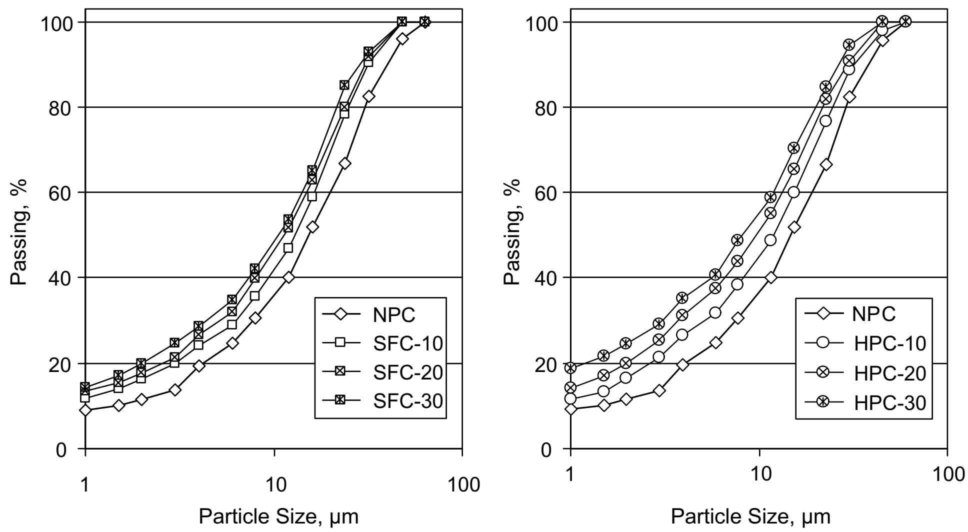

Fig. 3. Particle size distribution of the investigated cements.

4. Test results and discussion

4.1. Particle size distribution

The particle size distributions of investigated cements are presented in Fig. 3. Specific surface area and median size are given in Table 2. It was found that the application of SF and RSA significantly enlarged the specific surface area which continued to increase constantly with grinding. It is important to notice that the specific surface area was higher when SF was applied. At the same time, the median size was smaller in the case of RSA (Fig. 3).

4.2. Normal consistency and setting time

The samples of HP cements demonstrated the reduced normal consistency compared with the reference cement (Table 3). Following the trend specified for the surface area, the normal consistency of SF cement increased with the duration of intergrinding. Inverse results were observed when RSA was applied; due to additional grinding the normal consistency of HP cements was reduced (from 20% to 18.5%); this also resulted in a reduction of *W/C* required to produce the mortars of the same flow (Table 3). It is proposed that there is a strong correlation between these two parameters as well as a correlation between the normal consistency and the duration of grinding for HP cements. Therefore, the *W/C* of mortars can be actually calculated if the normal consistency is known. It was found that the setting times of the investigated cements were significantly extended because of the application of mineral additives in large volumes (i.e., 55% of clinker was replaced by the mineral additives). The subsequent intergrinding of SF cement further increased the initial and final setting times, which were extended by 47 min each. In contrast, intergrinding helped to decrease the setting times of HP cement by almost 50%. This is a clear sign of RSA–cement interaction and mechano-chemically induced changes within the system, which led to an acceleration of the hydration of HP cement.

Table 3
Compressive strength of mortars

Cement type	Normal consistency (%)	Setting time (min)		*S/C*	*W/C*	Compressive strength (MPa) at age (days)		
		Initial	Final			2	7	28
NPC	27.1	2:45	3:25	2.75	0.45	31.6	47.9	56.5
SFC-10	27.0	3:55	4:25	2.75	0.45	16.6	33.2	59.4
SFC-20	27.3	4:22	5:02	2.75	0.45	17.0	35.2	62.5
SFC-30	27.6	4:42	6:12	2.75	0.45	18.1	36.3	65.1
HPC-10	20.0	4:55	5:30	2.75	0.30	35.8	61.1	89.1
HPC-20	19.2	2:39	3:04	2.75	0.29	39.0	65.4	91.7
HPC-30	18.5	2:37	2:52	2.75	0.28	34.2	60.0	75.9

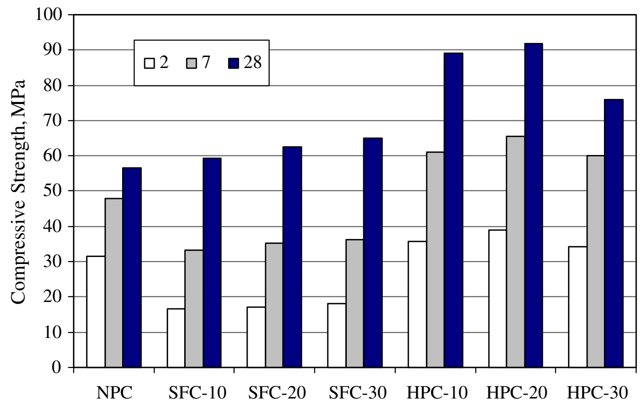

Fig. 4. Compressive strength of the investigated cements.

4.3. Compressive strength of mortars

The results of the compressive strength are summarized in Table 3 and Fig. 4. According to the obtained results, the application of SF helps to improve the 28-day compressive strength of cement with high volumes of GGBFS, up to levels exceeding NPC values by 15% (and even further increase after this age could be expected). In spite of this, SFC had a lower strength at early ages compared with NPC: only 57% and 76% at the age of 2 and 7 days, respectively. This delay of hardening could be explained by the use of high volumes of mineral additives (45% of GGBFS and 10% of SF). The additional intergrinding helped to increase the 28-day strength of SF cement by approximately 10% due to MCHA [4–6]. The application of RSA results in high-early strength cement with a compressive strength about 50% higher compared with SF cement. This difference is even much higher at early ages. The 7-day compressive strength of HP cement is about 16% higher than the 28-day strength of reference NPC (56.5 MPa). For HP cement, it was found that the intergrinding had an optimum duration of 20 min. This resulted in an HP cement with a maximum compressive strength at all ages of hardening (Table 3). Remarkable strength (91.7 MPa) was obtained by the optimized HP cement at the age of 28 days (62% higher than the reference NPC).

5. Conclusions

1. The test results demonstrated that the specific surface area of HVMA cements containing SF or RSA steadily increased with grinding. The specific surface area was higher when SF was applied; and the median size was smaller in the case of RSA.
2. The application of RSA reduced the normal consistency of the investigated HVMA cements. The normal consistency of SF cement increased with the time of intergrinding. Inverse results were observed when RSA was applied: MCHA resulted in a reduction of the normal consistency of HP cements.
3. The setting time of the investigated SF and HP cements increased significantly because of the incorporation of large volumes of mineral additives. It was recognized that the setting time was further extended with the intergrinding of SF cement. Due to the RSA–cement interaction and mechano-chemical changes in the system, MCHA helped to shorten the setting time of HP cements to the levels of NPC.
4. It is important to notice that the application of MCHA helped to improve the properties of cements containing large volumes of granulated blast furnace slag and modifying admixtures (SF or RSA). It is proposed that the properties of cement could be further improved by the application of more effective vibro-mills to facilitate MCHA.
5. It was found that the application of SF cannot overcome the hardening delay of HVMA cement with 45% of BFS; and, therefore, was not effective at early ages. Nevertheless, SF helped to improve the 28-day compressive strength of HVMA cement containing 45% of BFS to levels exceeding NPC and a further increase in ultimate strength could be expected.
6. The application of RSA was very effective and resulted in HVMA cement, which yielded a high compressive strength at all ages of hardening. It was found that when RSA was applied, the duration of MCHA had an optimum of 20 min. The 28-day compressive strength of 91.7 MPa was demonstrated by the optimized HVMA cement containing RSA. It was demonstrated if excessive intergrinding exceeded the optimal level, that the hydration of HVMA cements at early stages was accelerated; however, at the cost of reduced strength.
7. Further research programs will concentrate on the investigation and quantification of the micro-structural changes within the RSA–BFS–NPC system due to MCHA.

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