

The development of high-strength mortars with improved thermal and acid resistance

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Abstract

Granulated blast furnace slag (GBFS) cement, containing up to 60% slag, is sometimes used in repair materials applied at intermediate temperatures of 150–300 °C. Low rate of strength development, especially at early ages, is considered a common disadvantage of repair mortars based on slag cement. The present research was oriented to improving a GBFS–portland cement binder for application as a repair material in the chemical industry when high thermal or acid resistance is required. It was found that the enhancement of GBFS–portland cement-based materials can be achieved with the help of silica fume (SF) and a superplasticizer (SP). The effect of different SPs on the compressive and flexural strength of SF–blast furnace slag–portland cement mortars was investigated. These mortars, in addition to high strength, demonstrate high thermal and acid resistance.

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1. Introduction

It is known that the performance of concrete can be significantly improved by using selected mineral additives and, especially, some industrial by-products [1–12]. Granulated blast furnace slag (GBFS), fly ash (FA), and silica fume (SF) are among the most effective mineral additives used in cement or concrete because of their cementitious or pozzolanic properties. These materials are often used in the formulations of repair materials [4,8–12].

The effect of GBFS, FA, and SF on the properties of mortars and concrete has been discussed in the literature [1–8]. The behavior of these materials can be significantly affected by the fineness of a mineral additive and also by the application of an effective superplasticizer (SP) [7]. To describe such a system, the idea of a modified multi-

component binder (MMCB) was proposed [7,8]. An MMCB includes a binder composed of portland cement (NPC), finely ground mineral additive (FA or GBFS), and a highly reactive powder component (usually SF), modified by an SP. The main idea of MMCB is to improve the pozzolanic potential or reaction ability of the mineral additives by fine grinding. Consequently, the mineral additives react quicker, avoiding the delay of the development of concrete strength at an early age. It was also proposed that the application of finely ground mineral additives (FGMA) as a component of the binder provides better packing in the NPC–FGMA system, especially when used in combination with SF and SP. As demonstrated in Ref. [7], better packing of MMCB results in low water demand and better fluidity of the cement paste.

In this report, the effects of finely ground GBFS and SF on the properties of mortars were investigated. The amount of finely ground GBFS in the MMCB was 50% and SF content varied from 5% to 15%. The compressive and flexural strength of plain mortars and mortars modified by

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SPs were determined. The thermal resistance within the range of 50–800 °C and acid resistance in 30% solution of HCl was investigated.

2. Experimental program

2.1. Materials

The portland cement (NPC) used in the experimental program was CEM I 42.5 [13]. The chemical composition of the cement is given in Table 1. The Bogue compound composition of the cement was calculated according to ASTM C 150 [14] and is also given in Table 1. The physical and chemical properties of finely ground GBFS (FGGBFS) and SF are presented in Table 1.

Three types of SPs were used in the experimental program at 0.5–1.5% of cement weight. They were polyacrylate polymer-based hyperplasticizer (HP), naphthalene formaldehyde sulphonate (SNF), and melamine formaldehyde sulphonate (SMF) SPs.

The sand used in the composition of mortars was standard RILEM Cembureau type according to TS 819 [15]. The water was regular tap water.

Table 1
Chemical analysis and physical properties of the cementitious materials

	Portland cement	Blast furnace slag	Silica fume
<i>Chemical analysis</i>			
SiO ₂	19.80	40.7	90.00
Al ₂ O ₃	5.61	11.9	0.40
Fe ₂ O ₃	3.42	0.4	0.36
CaO	62.97	35.4	1.63
MgO	1.81	8.99	1.02
SO ₃	2.86	–	0.44
Na ₂ O	0.47	–	0.50
K ₂ O	0.87	–	2.28
Loss on ignition	0.36	–	3.03
<i>Bogue composition</i>			
C ₃ S	51.32	–	–
C ₂ S	19.25	–	–
C ₃ A	10.12	–	–
C ₄ AF	9.89	–	–
<i>Physical properties</i>			
Blaine surface area, m ² /kg	341	415	20000
Specific gravity, kg/m ³	3.15	2.90	2.25
Setting time, min			
Initial	130	–	–
Final	160	–	–
Compressive strength, MPa			
2 days	23.7	–	–
7 days	39.9	–	–
28 days	46.4	–	–

2.2. Research program

The experimental program included three main parts:

- investigation of the compressive and flexural strength of SF–FGGBFS–NPC-based mortars at different SF dosages, SP types, and sand-to-cement ratios (S/C);
- investigation of the thermal resistance of SF–FGGBFS–NPC-based mortars modified with HP within the temperature range of 50–800 °C;
- investigation of acid resistance (by comparison of weight loss) of SF–FGGBFS–NPC-based mortars modified with HP in 30% solution of HCl.

2.3. Notations used

The following notations were used in the experimental program:

- NPC-* reference mix;
- H*-* SF–FGGBFS–NPC binder modified with HP;
- N*-* SF–FGGBFS–NPC binder modified with SNF;
- M*-* SF–FGGBFS–NPC binder modified with SMF.

The numbers after the notations indicate the SF content in the binder. For the S/C an additional notation was used; and the letters S or R were used to specify S/C of 2.75 or 1, respectively.

2.4. Mix proportioning

The properties of 12 different mixtures were investigated. These were 2 reference mortars, 2 mortars with an SNF-based SP containing 10% of SF, 2 mortars with an SMF-based SP containing 10% of SF, and 6 mortars modified by HP with 5, 10, and 15% of SF. Except for the reference mortars, FGGBFS content was 50% and SP dosage was 10% of SF (corresponding to an SP dosage of 0.5%, 1.0%, and 1.5% of cement weight for mixes containing 5%, 10%, and 15% SF, respectively).

The S/C used was 2.75 and 1. The water content for each mix was determined by the flow test according to ASTM C 109 [16] in order to provide the standard workability for all mixes. The mix proportions are given in Tables 2 and 3.

2.5. Preparation of the specimens

The SF–FGGBFS–NPC-based binder was prepared by the intergrinding of the compositions in a laboratory ball mill. The total amount of cement was 8 kg and the weight of the grinding media was 120 kg. Grinding time was 30 min. After grinding, the manufactured cement was placed in plastic bags, sealed, and stored until testing.

The SP admixture was premixed with the total amount of water before application. The mortar mixtures were prepared in accordance with ASTM C 109 [16]. The flow table

Table 2
Flexural strength of investigated mortars

Mix type	SF, %	FGGBFS, %	SP, %	S/C	W/C	Flexural strength, MPa, at age, days		
						7	28	90
NPC-S	0	0	0.00	2.75	0.42	8.0	10.1	11.0
NPC-R	0	0	0.00	1.00	0.30	13.0	14.0	14.2
H5/50-S	5	50	0.50	2.75	0.29	9.0	11.0	13.2
H10/50-S	10	50	1.00	2.75	0.25	11.1	16.1	18.4
H15/50-S	15	50	1.50	2.75	0.25	11.2	16.5	19.4
H5/50-R	5	50	0.50	1.00	0.21	15.4	16.9	18.7
H10/50-R	10	50	1.00	1.00	0.17	15.2	18.5	20.9
H15/50-R	15	50	1.50	1.00	0.17	14.8	19.1	20.8
N10/50-S	10	50	1.00	2.75	0.25	10.2	14.5	18.9
N10/50-R	10	50	1.00	1.00	0.17	12.8	18.7	22.5
M10/50-S	10	50	1.00	2.75	0.25	6.9	10.9	11.8
M10/50-R	10	50	1.00	1.00	0.17	16.0	18.5	22.4

was used to adjust the flow within 105–115 mm. The mortar mixtures were cast into three-gang prism molds, each 40×40×160 mm in accordance with ASTM C 348 [17]. The obtained specimens were used in the tests of strength and thermal resistance.

For the acid resistance test, the specimens were cut with a masonry saw to obtain 40×40×40-mm cubic specimens. Following this, the four sides of the specimens were covered with an epoxy coating to ensure a one-dimensional corrosion process.

2.6. Curing of the specimens

Immediately after the compaction of mortars, the molds were placed in a humidity cabinet for 24 h at a relative humidity of 90–95% at 20 °C. After this period, the specimens were removed from the molds and kept in water until the testing day.

2.7. Experimental methods

The flow test was conducted for mortars to specify the required water content. The flexural and compressive strength tests of investigated mortars were performed at 7,

28, and 90 days. For flexural strength tests, three specimens from each mix were prepared and tested by one-point loading based on ASTM C348 [17]. Compressive strength tests were conducted using six specimens obtained after the flexural strength test as per ASTM C349 [18]. The results indicated are the average of the three specimens for the flexural strength and the average of the six specimens for the compressive strength values.

The thermal resistance of the mortars was assessed by the effect of high temperature (up to 800 °C) on strength. After 28 days of hardening in water, mortar samples were dried for 48 h in an oven at 50 °C. After drying, the specimens were placed in a muffle furnace and step-by-step increase of temperature was applied. The time interval for each step was 24 h; and the temperature increment for each step was 100 °C, starting at 100 °C and going to 800 °C. After each step, three specimens were picked from the furnace and the compressive strength of these specimens was determined after cooling. The criterion of 20% decrease in strength compared with 50 °C strength was used as a thermal resistance limit.

The water absorption of the mortars was determined by using oven-dry (at 100 °C) specimens. The specimens were immersed in water and their weight increase was measured

Table 3
Compressive strength of investigated mortars

Mix type	SF, %	FGGBFS, %	SP, %	S/C	W/C	Compressive strength, MPa, at age, days		
						7	28	90
NPC-S	0	0	0.00	2.75	0.42	48.4	52.9	66.8
NPC-R	0	0	0.00	1.00	0.30	69.5	79.2	81.1
H5/50-S	5	50	0.50	2.75	0.29	52.8	67.6	94.9
H10/50-S	10	50	1.00	2.75	0.25	63.9	97.9	126.3
H15/50-S	15	50	1.50	2.75	0.25	53.6	109.0	134.4
H5/50-R	5	50	0.50	1.00	0.21	75.3	95.8	114.1
H10/50-R	10	50	1.00	1.00	0.17	87.9	107.5	138.5
H15/50-R	15	50	1.50	1.00	0.17	84.6	123.2	142.5
N10/50-S	10	50	1.00	2.75	0.25	65.7	104.7	115.8
N10/50-R	10	50	1.00	1.00	0.17	87.2	123.1	144.3
M10/50-S	10	50	1.00	2.75	0.25	41.1	80.2	88.9
M10/50-R	10	50	1.00	1.00	0.17	81.6	105.3	113.6

until complete saturation of the specimens. Absorption was calculated as a percentage of dry weight.

Cubic specimens with the four sides sealed with epoxy were placed in an acid-resistant plastic container with a 30% HCl solution. Every 7 days, the samples were weighed to detect the weight change, and every 14 days acid solution was replaced in order to keep a constant pH. Investigations were performed within 5 weeks or until complete destruction of the specimens. Acid resistance was considered as the ability of a specimen to keep its constant weight, length, and shape during the test.

3. Test results and discussion

3.1. Flow and water requirement

The water content and flow values were tested at the stage of mortar preparation. The corresponding water-to-cement ratio (W/C) is given in Tables 2 and 3. The flow tests confirmed the possibility of producing mortars with a very low W/C. According to test results, all types of investigated SPs (SMF, SNF, and HP) allow a significant reduction of the W/C. The W/C was reduced to 0.17 and 0.25 for mortars, with S/C of 1 and 2.75, respectively.

3.2. Flexural strength

The results of the flexural strength tests are summarized in Table 2. The flexural strength of SF-FGGBFS-NPC-based mortars modified with SP is higher when compared with reference mortars at all ages of hardening. The 28-day flexural strength is improved by an increase in SF content up to 15%: 16.5 and 19.1 MPa for mortars, with S/C of 2.75 and 1, respectively. Still, mortars with 10% of SF have demonstrated similar values; therefore, 10% SF content was considered sufficient and used in the subsequent tests. Note that all tested SPs had quite a similar performance at S/C of 1 (18.5–18.7 MPa), whereas the application of HP was the most effective at S/C of 2.75 (16.1 MPa). It was found that

Compressive Strength, MPa

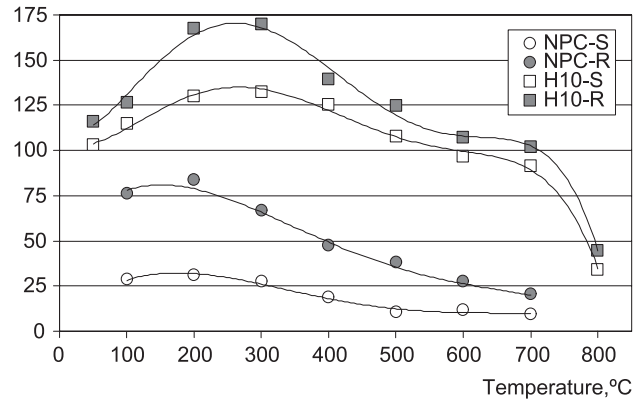


Fig. 2. The effect of high temperature on compressive strength.

when HP was applied there was no considerable gain in flexural strength after 28 days of hardening; in contrast, the application of SNF- and SMF-based SP yielded an additional increase in flexural strength at the age of 90 days (to 22.5 MPa).

3.3. Compressive strength

The results of the compressive strength tests of investigated mortars are summarized in Table 3 and Fig. 1. At all ages of hardening, the SF-FGGBFS-NPC-based mortars modified with SP demonstrated higher compressive strength than reference mortars. The difference in strength increases significantly when S/C is reduced from 2.75 to 1. The 28-day compressive strength is improved by an increase in SF content up to 15%, giving 109.0 and 123.2 MPa for mortars with S/C 2.75 and 1, respectively. As for compressive strength, SNF-based SP had the best performance (at SF content of 10%) yielding mortars with 104.0 and 123.1 MPa for S/C of 2.75 and 1, respectively. Still, the application of HP in mortars with S/C of 2.75 produced the best compressive strength at the age of 90 days (126.3 MPa).

The W/C is the most important parameter governing compressive strength (Fig. 1). It is important to note that the trendline based on the obtained strength data of SF-FGGBFS-NPC-based mortars could be considered as an extension of the line connecting the NPC values to the area of low W/C. It supports the assumption proposed in Ref. [7] that the pozzolanic activity of SF is approximately equal to the strength of the cement used and the microfiller effect is an ability of SF to reduce W/C (when SP is present) due to the better packing of the system.

3.4. Thermal resistance

The compressive strength of SF-FGGBFS-NPC-based mortars modified with HP after the thermal treatment up to 800 °C is presented in Fig. 2. The maximum compressive strength was found at 300 °C with values of 132.1 and 169.6 MPa for S/C of 2.75 and 1, respectively. The compressive

Compressive Strength, MPa

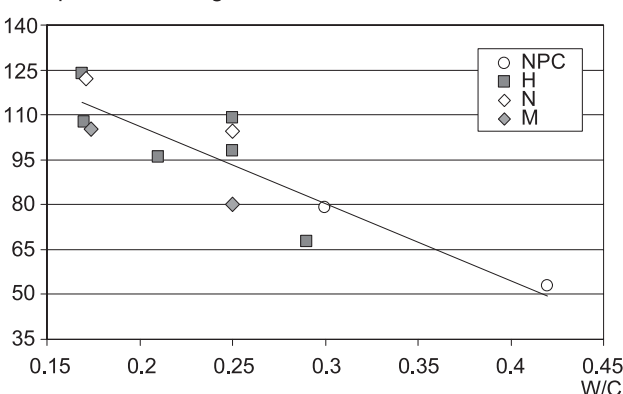


Fig. 1. The effect of W/C on compressive strength.

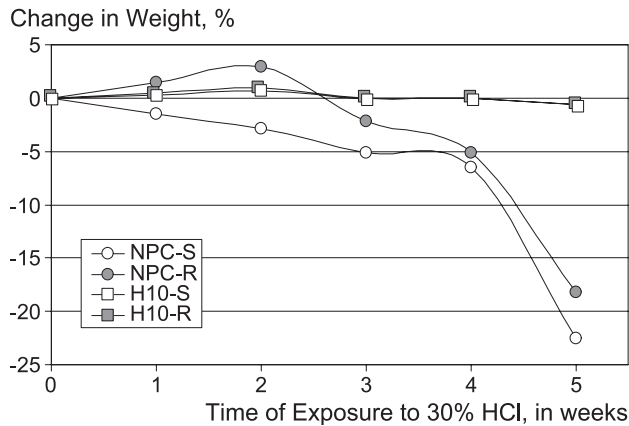


Fig. 3. Acid resistance of investigated mortars.

strength of the reference mortars at this temperature was 27.6 and 66.6 MPa for S/C of 2.75 and 1, respectively. The 20% loss of the compressive strength limit was achieved by SF-FGGBFS-NPC-based mortars only at 700 °C with values of 91.1 and 101.8 MPa for S/C of 2.75 and 1, respectively.

It was observed that the thermal treatment of reference mortars with S/C of 2.75 leads to more than 20% reduction of compressive strength at 100 °C. After treatment at 300 °C, the reference mortars with S/C of 1 passed the 20% limit (Fig. 2).

3.5. Water absorption

Due to extremely low W/C, the investigated mortars demonstrated very low water absorption. The water absorption of SF-FGGBFS-NPC-based mortars modified by HP was less than 1% (0.8% and 0.5% for mortars with S/C 2.75 and 1, respectively) compared with 4.6–5.6% water absorption of reference mortars.

3.6. Resistance to acid attack

The results of the acid resistance test are presented in Fig. 3. The SF-FGGBFS-NPC-based mortars modified by HP showed excellent resistance to acid attack. After 5 weeks of exposure in a 30% HCl solution, the investigated mortars lost only 0.6% of their weight. The reference mortars lost more than 5% weight after 4 weeks of exposure; and after 5 weeks of testing these mortars were completely destroyed (Fig. 3).

4. Conclusions

Based on the research the following conclusions could be made:

1. The application of SPs significantly reduces the water demand of SF-FGGBFS-NPC-based mortars; this

helps to produce mortars of the required workability at very low W/C.

2. The optimum SF content in the composition of SF-FGGBFS-NPC binder was found to be 15%. Still, 10% of SF is sufficient to produce mortars of high compressive and flexural strength at all ages of hardening.
3. It is confirmed that the SP is effective at a dosage of 10% of SF weight. The application of SP and the subsequent reduction in W/C results in mortars of high compressive and flexural strength. The best performance was demonstrated by HP (flexural strength) and SNF-type SP (compressive strength). The application of HP resulted in 28-day compressive strength of 97.9 and 123.2 MPa (at S/C of 2.75 and 1); at the same time the flexural strength of 16.1 and 18.5 MPa was achieved at S/C of 2.75 and 1, respectively.
4. SF-FGGBFS-NPC-based mortars modified with HP demonstrated high thermal resistance within the temperature range of 100–700 °C; moreover, an improvement of compressive strength of these mortars (to the level of 132.1–169.6 MPa) can be achieved by thermal treatment at 200–300 °C.
5. SF-FGGBFS-NPC-based mortars modified with HP demonstrated very low water absorption (5–10 times less compared with reference).
6. SF-FGGBFS-NPC-based mortars modified with HP showed very high resistance to HCl (30% concentration).
7. The SF-FGGBFS-NPC-based mortars modified by SP demonstrated the following properties: high strength, improved thermal resistance, and resistance to acid attack. Therefore, they could be classified as “high-performance cement-based materials.” These formulations can be recommended for application as a repair material in the chemical industry when high thermal or acid resistance is required.

References

- [1] P. Zia, M.L. Leming, S.H. Ahmad, High-Performance Concretes: A State-of-the-Art Report, SHRP-C/FR-91-103, Strategic Highway Research Program, National Research Council, Washington, 1991.
- [2] V.M. Malhotra, High-performance high-volume fly ash concrete, in: B.V. Rangan, A.K. Patnaik (Eds.), Proceedings of the International Conference on High Performance High-Strength Concrete: Material Properties, Structural Behavior and Field Application, Curtin University of Technology, Perth, 1998, pp. 97–122.
- [3] P.K. Mehta, Pozzolanic and cementitious by-products in concrete—another look, in: V.M. Malhotra (Ed.), Proceedings of the Third CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, SP-114, ACI, Trondheim, 1989, pp. 1–14.
- [4] S.M. Royak, G.S. Royak, Special Cements, Stroyizdat, Moscow. In Russian.
- [5] W. Reiser, Blended and custom made cements—the future in high competitive markets, in: H. Ashraf (Ed.), Proceedings of the International Cement Conference—Cemtech, Holbrooks Printers, Istanbul, 1996, pp. 124–152.

- [6] J.H. Kim, The economic viability of Portland blast furnace slag cement, in: H. Ashraf (Ed.), *Proceedings of the International Cement Conference—Cemtech*, Holbrook Printers, Istanbul, 1996, pp. 191–204.
- [7] K. Sobolev, High-strength concrete with low cement factor, PhD dissertation, Chemical Admixtures Lab, Scientific and Research Institute of Concrete and Reinforced Concrete, Moscow, 1993 (in Russian).
- [8] V.G. Batrakov, E.S. Silina, K. Sobolev, N.F. Zigulev, Recommendations on Production and Application of the High-Strength and Super-High-Strength Highly Dense Concrete with Microsilica, NIIZhB-Scientific and Research Institute of Concrete and Reinforced Concrete, Moscow. In Russian.
- [9] A.A. Al-Manaseer, E.B. Aquino, H. Kumbardi, Properties of concrete containing ultimax rapid-setting hydraulic cements, *ACI Mater. J.* 96 (5) (1999) 529–535.
- [10] K. Sobolev, M. Arikan, High volume mineral additive ECO-cement, *Am. Ceram. Soc. Bull.* 81 (1) (2002) 39–43.
- [11] K. Sobolev, High performance cement: solution for next millennium, *Mater. Technol.* 14 (4) (1999) 191–193.
- [12] K. Sobolev, The effect of complex admixtures on cement properties and development of a test procedure for the evaluation of high-strength cements, *Adv. Cem. Res AC15* (2) (2003) 65–75.
- [13] EN 197-1, Cement—Part 1 Composition, specifications and conformity criteria for common cements, European Standard, European Committee for Standardization, 1994.
- [14] ASTM C 150, Standard specification for portland cement, in: *Annual Book of ASTM Standards*, vol. 04.01, American Society for Testing and Materials (ASTM), Philadelphia, 1993.
- [15] TS 819, RILEM—Cembureau Standard Sand, Turkish Standard Institute (TSE), Ankara, Turkey, 1989.
- [16] ASTM C 109, Compressive strength of hydraulic cement mortars (using 2-in. or 50-mm cube specimens), in: *Annual Book of ASTM Standards*, vol. 04.01, American Society for Testing and Materials (ASTM), Philadelphia, 1993.
- [17] ASTM C 348, Flexural strength of hydraulic cement mortars, in: *Annual Book of ASTM Standards*, vol. 04.01, American Society for Testing and Materials (ASTM), Philadelphia, 1993.
- [18] ASTM C 349, Compressive strength of hydraulic cement mortars (using portions of prisms broken in flexure), in: *Annual Book of ASTM Standards*, vol. 04.01, American Society for Testing and Materials (ASTM), Philadelphia, 1993.