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Properties of blastfurnace cements (CEM III/A, B, C) based on Portland cement clinker, blastfurnace slag and cement kiln dusts

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ACCEPTED MANUSCRIPT PROPERTIES OF BLASTFURNACE CEMENTS (CEM III/A, B, C) BASED ON 1 PORTLAND CEMENT CLINKER, BLASTFURNACE SLAG AND CEMENT KILN 2 DUSTS 3 Zehrudin Osmanović^{a,*}, Nedžad Haračić^b, Jelica Zelić^c 4 5 ^a Faculty of Technology, University of Tuzla, T. Markovića 1, 75 000 Tuzla, Bosnia and 6 Herzegovina 7 ^b Kakanj Cement Works, Heidelberg Cement Group, S. ef. Merdanovića 146, 72240 Kakanj, 8 Bosnia and Herzegovina 9 ^c Faculty of Chemistry and Technology, University of Split, Teslina 10/V, 21000 Split, 10 11 Croatia 12 *Corresponding author: Tel: 0038761954760 13 E-mail address: zehrudin.osmanovic@untz.ba 14 15

16 ABSTRACT

This study has examined the effectiveness of characteristically different cement kiln dusts 17 (CKDs) as a partial replacement for the ground granulated blastfurnace slag (GGBFS) in the 18 development and production of three types of blastfurnace cements (CEM III/A, B, C) 19 according to the standard EN 197-1. 27 CEM III cement blends, 9 blends per type of cement, 20 21 i.e., CEM III/A, CEM III/B and CEM III/C, were prepared in the laboratory mill from industrial starting materials (Portland cement clinker, gypsum, GGBFS, CKDs). The addition 22 of gypsum as the setting regulator was fixed at 4 mass % in all blends studied. The content of 23 both CKDs (cement clinker dust and cement filter dust) as slag replacements was 4 mass % in 24 all CKD blends studied. The ordinary Portland cement (OPC) type CEM I 42.5N was used as 25 26 the control cement. The results have shown that the chemical composition and chemical and physical properties of prepared CEM III/A, B, C cement blends meet the EN 197-1 27

requirements. Strength development in these cement blends is obviously related to the Portland cement clinker-to-GGBFS ratio. When compared to OPC, the blastfurnace cement developed lower compressive strength at early ages, but equal or higher at later ages in more cases, i.e., all 9 CEM III/A and 7 CEM III/B cement blends meet, while no CEM III/C cement blend meets the EN 197-1 requirements for standard compressive strength Class 42.5N. From the perspective of strength, the presence of the cement clinker dust is more effective than that of the cement filter dust due to their different chemical and mineralogical compositions.

8 Keywords: Blastfurnace cement (CEM III/A, B, C), GGBFS, CKDs, chemical and physical

9 properties, mechanical strength, mortars

10

11 **1. Introduction**

Ground granulated blastfurnace slag (GGBFS), obtained as a by-product in the production of 12 metallic iron, is granulated, rapidly cooled, and therefore predominantly glassy, basic slag. 13 The slag contains the same oxides (SiO₂, Al₂O₃, CaO) that make up Portland cement but in 14 different proportions. According to the European cements standard EN 197-1, at least two-15 thirds of the slag by mass must be glass and the mass ratio (CaO+MgO)/SiO₂ must also be 16 greater than 1.0 [1]. The latent hydraulic properties of slag are activated in the presence of 17 18 cement clinker, sulphates or calcium hydroxide (but other alkaline substances are also effective). With all activators, the calcium silicate hydrate or C–S–H phase is produced as the 19 hydration product which governs the hardening. Clinker activation is used in the manufacture 20 of Portland slag cements and blastfurnace cement, and sulphate activation in the manufacture 21 22 of super sulphate cement. Generally, the rate of hardening of slag cement is somewhat slower than that of ordinary Portland cement (OPC) during the first 28 days, but increases thereafter 23 24 so that at 12 months the strength becomes close to or even exceeds that of OPC [2]. GGBFS

1 can be used as a direct replacement for OPC on one-to-one basis by mass. Replacement rates for GGBFS vary from 30 mass % to up to 85 mass %. In general, up to 50 mass % GGBFS is 2 used in most applications. However, higher replacement rates up to 85 mass % GGBFS are 3 used in special applications either to improve the durability of concrete in aggressive 4 environments or to reduce heat of hydration in massive concrete structures [3]. Nowadays the 5 GGBFS is most widely used as the main constituent to produce high-performance Portland 6 7 cement blends that are more economical and environmentally friendly. The EN 197-1 differentiates some main categories of cements containing different proportions of GGBFS, 8 9 i.e., Portland slag cement (CEM II), Blastfurnace cement (CEM III) and Composite cement (CEM V). The Portland slag cement type (CEM II) exists in two classes designated as CEM 10 II/A-S and CEM II/B-S in which the maximum content of GGBFS is 20 and 35 mass %, 11 respectively. There are two classes of Composite cements CEM V designated as CEM V/A 12 and CEM V/B in which, in addition to cement clinker and pozzolana, the maximum content of 13 GGBFS is 30 and 50 mass %, respectively. Blastfurnace cements CEM III (where CEM III is 14 the designation for three types of blastfurnace cements A, B and C), in addition to Portland 15 cement clinker, contain between 36 and 95 mass % of GGBFS with subdivisions at 66-80 16 mass % of GGBFS [1]. Table 1 shows the composition of three types of blastfurnace cements 17 (BFSC). 18

19

 Table 1 Composition of blastfurnace cements (BFSC) [1]

20

According to EN 197-1, chemical requirements for blastfurnace cements CEM III/A, B, C limit the content of loss on ignition (LOI), insoluble residue (IR), sulphate (as SO₃), and chloride to 5.0 mass %, 5.0 mass %, 4.0 mass %, and 0.1 mass %, respectively. The alkali content (expressed as Na₂O-equivalent) is limited to the maximum value of (0.95–1.10), 2.00, and 2.00 mass % for CEM III/A, CEM III/B and CEM III/C, respectively. The specific

surface area must be not less than 4000 cm²/g. The expansion in Le Chatelier test for
 soundness must not exceed 10 mm [1].

Cement kiln dusts (CKDs) are finely divided particulate materials which have been produced 3 and carried on by combustion gases as a result of the movement of materials through the kiln 4 system during the production of Portland cement, and collected by the control device system 5 (e.g., cyclone, bag house, or electrostatic precipitator). The physical, chemical and 6 7 mineralogical composition of CKD is determined by raw feed used to produce clinker, type of kiln operation and fuel, and individual plant practices including the dust collection system. 8 9 With the exception of CKD collected from cement kiln exhaust gases, all the dusts have the same chemical composition as the raw feed [2]. Cement kiln dust is composed primarily of 10 11 variable mixtures of calcined and non-calcined feed materials, fine cement clinker, fuel combustion by-products, and alkali compounds. The relatively high alkali (Na₂O and K₂O) 12 and sulphate content of CKD is the predominant factor preventing its direct recycling with 13 cement raw materials in the kiln during cement production. Therefore, the use of CKDs in 14 cement mortars and concrete, as a potential replacement for either ordinary Portland cement 15 (OPC) or for blastfurnace slag cement (BFSC) is more effective [3-5]. In general, wide 16 variations observed in the chemical composition of CKDs limit their possible applications. 17 The presence of alkali, sulphate and free lime in CKDs may play an important role in 18 activation of aluminosilicate-containing materials, such as fly ash or slag, when CKDs are 19 used in blended cements [6]. The European cement standard EN 197-1 allows the use of 20 inorganic material substances from clinker production as a minor additional constituent to 21 cement up to 5 mass % [1]. 22

The utilization of CKDs in blended cements was a subject of many studies. Bhatty [7]
investigated the effectiveness of cement kiln dust (CKD) in blended cement systems using
ordinary Portland cement (OPC), five different CKDs, two different types of fly ash (Class F

1 and C), and GGBFS. He found that cements containing CKD alone had reduced strength, setting time, and workability, while the addition of fly ash to a CKD-OPC system lowered the 2 alkali content and resulted in improved strength. Shoaib et al. [8] evaluated the effect of 3 partial replacement (10, 20, 30, and 40 mass %) of "untreated" raw CKD, collected from 4 electrostatic precipitators, on mechanical properties of OPC, BFSC and sulphate resisting 5 Portland cement (SRPC). The authors found that the optimum quantity of CKD replacement 6 7 which could be used in the manufacture of these types of cements was not more than 30 mass %, 20 mass % and 10 mass % for SRPC, BFSC and OPC, respectively. Heikal et al. 8 [9] investigated the effect of the partial replacement (2.5, 5.0, 7.5 and 10.0 mass %) of by-9 pass cement dust on physical and rheological properties of Portland cement clinker-GGBFS 10 11 composites. Three blends of slag cements were prepared with Portland cement clinker-to-GGBFS ratios of 70/30, 50/50, and 30/70, respectively. The authors found that by-pass 12 cement dust, which contained high amounts of alkalis (3.32 mass %) and CaO (42.99 mass 13 %), affected physical and rheological properties of Portland cement clinker-GGBFS 14 composites both by its content and mix composition. The addition of 2.5 mass % by-pass 15 cement dust to blends containing up to 50 mass % GGBFS retarded initial and final times and 16 accelerated the final setting times of blend containing 70 mass % GGBFS. With the addition 17 of 5.0 mass % by-pass cement dust to blend containing 70 mass % GGBFS the initial and 18 final setting times were extended. Higher additions of by-pass cement dust (from 7.5 to 10.0 19 mass %) accelerated the final setting times. According to these authors, this may be due to the 20 increased amount of excess alkalis in by-pass cement dust, which acts as a good activator for 21 the hydration of the hydraulic latent GGBFS. Namely, during alkaline activation, the network 22 structure of GGBFS disintegrated and silicate and aluminate ions were taken into the solution, 23 which resulted in the increase of the hydration rate. Konsta-Gdoutos and Shah [10] 24 investigated the possibility of utilizing CKDs from different sources as an activator of 25

GGBFS in terms of hydration products, time of setting, rates of heat evolution and strength 1 development. The authors reported that the combination of both chemical and physical 2 characteristics of CKDs was critical in controlling the mechanisms of GGBFS activation, the 3 properties of hydration products, and the strength development rate. Maslehuddin et al. [11] 4 evaluated the effect of 0, 5, 10 and 15 mass % CKD replacements on the compressive strength 5 development and durability characteristics of the ASTM C 150 Type I (ordinary Portland 6 7 cement) and Type V (high sulphate resistance cement) cements. According to authors, the limit value of CKD replacement is 5 mass % from the aspect of both durability and strength. 8 9 Higher CKD replacements (10 and 15 mass %) affected chloride permeability and electrical resistively, suggesting the risk of reinforcement corrosion. Amin et al. [12] studied the effect 10 11 of calcined CKD content and the calcination temperature on the hydration properties of GGBFS. They concluded that the activation of GGBFS increased with the increasing content 12 13 and calcination temperature of the CKD. A similar conclusion was reached in a study conducted by El-Didamony et al. [13]. The authors found that the activation of GGBFS 14 15 increased with the firing temperature of kiln dust and the amount of added anhydrite. Kiln 16 dust (calcined at 1300 °C) with the addition of 15 mass % of anhydrite was found to be suitable for the production of super sulphate cement. Abo-El-Enein et al. [14] investigated the 17 effect of CKD and kiln meal additions on strength development of the BFSC. They found that 18 19 both additions accelerated the hydration rate but lowered compressive strength when compared to BFSC. 20

The present research is the first attempt to investigate the effectiveness of characteristically different cement kiln dusts (CKDs) that were used as a partial replacement for the GGBFS in both the development and manufacture of three types of blastfurnace cements CEM III/A, B, C according to the EN 197-1 standard. Physical and chemical, and mechanical characteristics of these blends were studied with respect to the normal consistency

and setting times, soundness, and mechanical strength. The optimum compositions suitable
 for the production of CEM III/A, B, C cements containing CKDs (the EN-197 standard
 strength Class 42.5) were established.

4

5 2. Experimental procedure

6 2.1. Materials

Materials used in this research were a Portland cement clinker and two different types of 7 CKDs (supplied from the Kakanj Cement Works, Heidelberg Cement Group, Kakanj, B&H), 8 granulated blastfurnace slag (obtained from the BH Steel Arcelor Mittal Zenica, B&H), and 9 gypsum (provided from the Komar Gypsum Plant, Donji Vakuf, B&H). Very fine powders of 10 both untreated raw CKD or filter dust (herein referred as CFD), whose composition 11 corresponded to non-calcined feed materials, and clinker dust (herein referred as CKD), 12 13 which consisted predominantly of cement clinker materials, were collected by a bag house from the raw mill and the clinker cooler, respectively. The mineralogical composition of 14 15 Portland cement clinker, determined by electron microscopy (EM Olympus BX 51), was 65.5 mass % C₃S, 9.4 mass % C₂S, 9.2 mass % C₃A and 11.0 mass % C₄AF. In addition to clinker 16 minerals, it contained periclase (MgO), lime (CaO), and arcanite (K₂SO₄) in the proportion of 17 4.9 mass %. X-ray diffraction (XRD) analysis (Fig. 1) indicated that the granulated 18 blastfurnace slag (GGBFS) consisted of 90 mass % of glassy phase [15]. The chemical 19 20 composition of materials used was determined by X-ray fluorescence (XRF) spectroscopy (Philips Cubix XRF with Super Q Program), and are shown in Table 2. 21

- 22
- 23 24

Figure 1 XRD plots of materials used in this study: GGBFS (black plot), filter dust (blue plot), Portland cement clinker (red plot), and clinker kiln dust (green plot) **[15].**

25

 Table 2 Chemical analysis of materials used (in mass %)

1 2.2. Specimens and testing

According to the EN 197-1 standard, CEM III/A, B, C 42.5N blastfurnace cement (BFSC) 2 blends were prepared. The content of GGBFS and Portland cement clinker varied between 35 3 and 91 mass %, and between 5 and 57 mass %, respectively. The content of gypsum as the 4 setting regulator was fixed at 4 mass % in all blends studied. The GGBFS replacement by 5 6 both CKDs (cement clinker dust and cement filter dust) was 4 mass % in all CKD blends 7 studied. 27 CEM III/A, B, C blends, 9 blends for each of three types of the BFSC, were prepared. CEM III/A, CEM III/B and CEM III/C blends were designated U1 ... U9, U10 ... 8 U18, and U19 ... U27, respectively. Ordinary Portland cement (OPC), type CEM I 42.5N, 9 containing 96 mass % of Portland cement clinker and 4 mass % of gypsum, was used as the 10 control cement. Cement mixture proportions (in mass %) as well as the chemical composition 11 of the control OPC and all three types of CEM III/A, B, C 42.5N blends are shown in Tables 12 3, 4, 5 and 6, respectively. 13

The laboratory-prepared CEM III/A, B, C blends were produced by inter-grinding cement 14 clinker with GGBFS and the addition of gypsum, and either CKD or CFD in the ball mill to 15 the Blaine fineness of 4300 cm²/g [16]. As expected, the grinding ability of GGBFS is lower 16 than that of clinker, i.e., by increasing the slag content in BFSC blends, the time of grinding 17 increases. For example, in 2.0 kg BFSC blends the time of grinding increases from 130 min to 18 160 min and to 185 min for CEM III/A, CEM III/B and CEM III/C blends, respectively. The 19 specific gravity of all prepared cement blends, determined by pycnometer, was about (in 20 g/cm³): 3.10, 2.78–2.92 (average value 2.85), 2.69–2.76 (average value 2.72), and 2.61–2.68 21 (average value 2.64) for the control OPC, CEM III/A, CEM III/B and CEM III/C, 22 respectively. 23

1	Physical and chemical properties (the required water for normal consistency and Vicat setting
2	time, Le Chatelier volume expansion) of all CEM III/A, B, C cement blends were determined
3	in accordance with the standards of EN 196-3 [17]. Three series of CEM III/A, B, C mortar
4	samples and one control CEM I 42.5N mortar sample (40 x 40 x 160 mm in size) with water-
5	to-binder ratio of 0.5 were prepared in accordance with the standards of EN 196-1 [18].
6	Compressive and flexural strength development tests were carried out on mortar specimens in
7	accordance with the EN 196-1 standard [18] from triplicate specimens at the age of 2, 7, 28,
8	90, 180 and 365 days. All the reported results are the averages of three measurements.
9 10	Table 3 Mixture proportion of control, ordinary Portland cement (OPC), CEM I 42.5N, andblastfurnace cement, CEM III/A 42.5N, in mass %
11	Table 4 Mixture proportion of blastfurnace cement, CEM III/B 42.5N, in mass %
12	Table 5 Mixture proportion of blastfurnace cement, CEM III/C 42.5N, in mass %
13 14 15 16 17	Table 6 Chemical composition of control, ordinary Portland cement (OPC), CEM I 42.5N, and three types of blastfurnace cements CEM III/A, B, C prepared (where samples designated as U1 U9, U10 U18, and U19 U27 denote the CEM III/A, CEM III/B and CEM III/C, respectively), in mass %.
18	3. Results and discussion
19	3.1. Chemical and physical properties
20	The chemical composition of materials used as well as of the control OPC (CEM I 42.5N) and
21	three types of blastfurnace cements CEM III/A, B, C prepared are shown in Tables 2 and 6,
22	respectively. Results given in Table 2 indicate that GGBFS used contained, in addition to
23	CaO and MgO, significant amounts of SiO ₂ as a main constituent, but it met the requirements
24	of EN 197-1, i.e., the mass ratio (CaO+MgO)/SiO ₂ was greater than 1.0. Contrary to OPC, by
25	increasing the GGBFS content in CEM III/A, B, C the content of SiO ₂ and MgO increased but

1 the CaO content decreased. The clinker dust (CKD) collected from the cleaning system of clinker cooler generally differs in composition from the filter dust (CFD) that corresponds to 2 the raw meals only in its degree of calcination. Similar to Portland cement clinker, CKD 3 contained significant amounts of CaO (66.66 mass %) compared to CFD (43.21 mass % 4 CaO). Table 6 shows the chemical analysis and characteristic values (loss on ignition, 5 insoluble residue, sulphate content as SO₃, alkali content as Na₂O-equivalent, and chloride 6 content) of the control OPC (CEM I 42.5 N), and CEM III/A, B, C blends, determined 7 according to EN 196-2 [19]. In all 27 BFSC blends the average content of loss on ignition, 8 9 insoluble residue, sulphate content as SO₃, alkali content as Na₂O-equivalent, and chloride content was (in mass %): 1.81, 0.0024, 2.92, 0.40, and between 0.0014 and 0.0042, 10 respectively. These values are lower than the values specified by EN 197-1 [1]. 11

The water requirement for standard consistency and setting times of control OPC (CEM I 12 42.5N) and CEM III/A, B, C blends are shown in Figures 2 and 3, respectively. An average 13 14 value of the water requirement for all the 27 BFSC blends were varied in range of 26.0 to 28.2 % compared with 27.0 % for control OPC. This indicates that GGBFS affected the 15 consistency of BFSC and it decreased with increased in GGBFS content from 61 to 76 mass 16 % (U1 and U10 blends). However, by increasing of the GGBFS content to 91 mass % (U19 17 blend), the consistency increased (Fig. 2). The results show that addition of cement filter dust 18 (CFD) slightly decreased the water requirements for normal consistency when compared to 19 the cement clinker dust (CKD). The lower water requirements were noted in the U9, U17 and 20 U25 blends, i.e., in blends which, in addition to cement clinker, gypsum and CFD, contain 46, 21 22 64 and 87 mass % GGBFS, respectively. The higher water requirements was noted in the U14 and U24 blends, i.e., in blends which, in addition to cement clinker, gypsum and CKD, 23 contain 64 and 82 mass % GGBFS, respectively. The initial and final setting times of OPC 24 25 (CEM I 42.5N) and CEM III/A, B, C are showing in Fig. 3. The OPC reached initial set in

1 130 min whereas for the CEM III blends it was extended on average values of 211 min, 223 min, and 220 min for CEM III/A, CEM III/B, and CEM III/C, respectively. The average 2 values of final setting time in OPC and CEM III/A, B, C blends were 170, 279, 287, and 284 3 min, respectively. Significant increase in the final setting time, between 300 and 325 min, was 4 observed for the BFSC blends containing CFD (i.e., U7, U9, U16, and U18 blends). As 5 expected, the OPC (CEM I 42.5N) reached final setting time after 40 min of the initial set, 6 whereas for the CEM III/A, CEM III/B and CEM III/C blends were extended on 67.8 min, 64 7 min and 64 min, respectively. The increase in the initial and final setting time with the 8 decreasing of the water requirements for normal consistency in the BFSC-CFD blends 9 indicates a low hydraulic properties (low CaO content) of CFD in comparison with cement 10 clinker dust (CKD). The Le Chatelier volume expansion test was shown values of 0.5 mm for 11 all BFSC blends expect the U6, U9 and U12 blends with values of 3.0, 1.0 and 1.0 mm, 12 13 respectively. However, all obtained values were within the allowable value of 10 mm specified by EN 197-1 [1]. 14

15

Figure 2 Water required for standard consistency for all analysed cement blends.

16

Figure 3 Initial and setting times for all analysed cement blends.

17

18 3.2. Mechanical strength development

The development of compressive strength as a function of hydration time (2–365 days) of the control OPC mortar (CEM I 42.5N) and CEM III/A, B, C mortar blends is shown in Figures 4(a)–4(c). Generally, it can be seen that the compressive strength increases gradually with the curing time for all mortar samples. When compared to the OPC mortar, CEM III/A, B, C mortars show lower compressive strength during the first 28 days, but after that their strength increases considerably, so that at 12 months it becomes close to or even exceeds that of OPC.

1 The CEM III/A blend with the clinker-to-GGBFS ratio of 46/50 and with the addition of 4.0 2 mass % of gypsum (the U3 sample) developed the highest 365-day compressive strength of 87.60 MPa when compared to the OPC strength of 75.20 MPa and to all BFSC blends. The 3 BFSC blends with 4.0 mass % of gypsum, the clinker-to-GGBFS ratio of 57/35 and the 4 addition of either 4.0 mass % of CKD (the U5 sample) or 4.0 mass % of CFD (the U8 sample) 5 reach higher values of the 365-day compressive strength, in the range of 85.60 MPa and 80.20 6 MPa, respectively, than the OPC mortar (75.20 MPa). However, at the age of 28 days, the 7 compressive strength of all CEM III/A blends was lower, ranging from 45.80 MPa to 60.00 8 MPa, when compared to the control OPC strength of 66.90 MPa. These values, however, meet 9 10 standard strength for Class 42.5, which stipulates the standard 28-day strength of cement in the range between 42.5 MPa (minimum) and 62.5 MPa (maximum), as defined in EN 197-1. 11 When compared to OPC, the increase of the GGBFS content in CEM III/B blends results in 12 13 the lowering of both 28- and 365-day compressive strength, but the values obtained meet, in most cases, the standard strength for Class 42.5. For example, with the clinker-to-GGBFS 14 15 ratio in the range between 28/68 and 28/64, the U11, U14 and U17 mortar samples developed strength ranging from 43.60 MPa to 70.20 MPa, 46.60 MPa to 73.10 MPa, and 40,00 MPa to 16 59.60 MPa at the age from 28 to 365 days, respectively. The compressive strength 17 development of all CEM III/C blends was always lower than that of OPC and of 18 CEM III/A, B blends and did not meet standard requirements for the strength Class 42.5. For 19 example, with the clinker-to-GGBFS ratio in the range between 14/82 and 14/78, the U20, 20 U23 and U26 mortar samples developed strength ranging from 31.30 MPa to 46.60 MPa, 21 22 36.10 MPa to 54.70 MPa, and 28.10 MPa to 40.20 MPa at the age from 28 to 365 days, respectively. The above results indicate that all 9 CEM III/A and 7 CEM III/B cement blends 23 meet the EN 197-1 requirements in terms of compressive strength, i.e., the EN-197 standard 24 strength Class 42.5, while no CEM III/C cement blend meets these requirements. 25

1	Alternatively, these CEM III/B and CEM III/C blends may be utilized to produce low early
2	blastfurnace cements [20].
3	
4	Figure 4(a) Compressive strength development of control CEM I cement mortar and
5	U1-U9 (CEM III/A) cement mortar blends.
6	Figure 4(b) Compressive strength development of control CEM I cement mortar and
7	U10-U18 (CEM III/B) cement mortar blends.
8	Figure 4(c) Compressive strength development of control CEM I cement mortar and
9	U19-U27 (CEM III/C) cement mortar blends.
10	
11	A similar trend due to different proportions of the cement clinker-to-GGBFS ratio and curing
12	time was also observed in the development of flexural strength, as shown in Figures
13	5(a)-5(c). Compared to OPC (the standard flexural strength at 28 days of 5.5 MPa), flexural

strength of all BFSC blends was lower at early ages (2 and 7 days), but equal or higher at later

ages (up to 28 days). For example, the flexural strength of the OPC, CEM III/A, CEM III/B

and CEM III/C was 6.8 MPa, 3.9–5.7 MPa, 3.6–4.4 MPa, and 2.9–3.8 MPa at 7 days, 8.4 MPa, 6.9–8.9 MPa, 7.5–8.2 MPa, and 5.3–9.4 MPa at 28 days, and 9.8 MPa, 9.3–10.8 MPa, 9.4–10.5 MPa, and 8.1–9.9 MPa at 365 days, respectively. When compared to the 28-day compressive strength of the same mortar samples (e.g., the U2, U5, U8 and U9 blends), the flexural strength of these mortars was higher than that of the OPC mortar, Figs. 4(a) and 5(a). Specifically, the addition of CFD had a more significant effect on the flexural strength development than the CKD addition even in the case of a higher GGBFS content of 46.0 mass

23 % (the U9 mortar sample).

15

Figure 5(a) Flexural strength development of control CEM I cement mortar and
 U1-U9 (CEM III/A) cement mortar blends.

Figure 5(b) Flexural strength development of control CEM I cement mortar and U10-U18 (CEM III/B) cement mortar blends.

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Figure 5(c) Flexural strength development of control CEM I cement mortar and U19-U27 (CEM III/C) cement mortar blends

From the results obtained it can be concluded that the strength development is obviously 6 related to the GGBFS content, i.e., to the clinker-to-GGBFS ratio. The CEM III/A mortars, 7 which contain between 35 and 61 mass % GGBFS, show equal or higher strengths than the 8 control OPC mortar after 180 and 365 days of hydration. However, as the GGBFS content 9 increases (e.g., in the range between 64-76 mass % and 78-91 mass % in CEM III/B and 10 11 CEM III/C blends, respectively) with the decreasing cement clinker content (e.g., in the range 12 between 20–28 mass % and 5–14 mass % in CEM III/B and CEM III/C blends, respectively) the compressive strength decreases. So, CEM III/C blends have a lower early and late strength 13 than the specified values. This indicates that cement clinker is mainly responsible for strength 14 development, i.e., the initial reaction of hydration is governed by the clinker fraction in the 15 BFSC. Moreover, the formation of nuclei of the calcium silicate hydrate or C–S–H phases 16 which have a higher CaO/SiO₂ ratio and are capable of growth (and can only be produced in 17 the presence of hydrating C_3S or cement clinker) have a certain importance in the activation 18 effect on slag. On the other hand, the hydration mechanism of a combination of GGBFS and 19 either Portland cement or Portland cement clinker is slightly more complex than that of 20 Portland cement or clinker alone. The hydration reaction involves the activation of GGBFS by 21 alkalis and sulphates to form its own hydration products. During its hydration, GGBFS in 22 23 BFSC consumes a varying proportion of Ca(OH)₂ produced during the hydration of the cement clinker fraction. The main hydration product of GGBFS is hydrated calcium silicate, 24 as the C-S-H gel, which is different from that formed in the Portland cement clinker 25 hydration and has a lower CaO/SiO₂ ratio which decreases with the increasing slag content. 26

For this reason it is justifiable to differentiate a latent hydraulic reaction, in which the
 consumption of Ca(OH)₂ is of secondary importance only, and a pozzolanic reaction [2].

The results obtained in this study indicate that with the proper mix design, i.e., the clinker-to-3 GGBFS ratio, both CKDs (cement clinker dust, CKD, and cement filter dust, CFD) can be 4 successfully utilized as a replacement for GGBFS. Generally, the replacement of GGBFS by 5 CKD is more effective than the replacement by CFD. A possible explanation could be that 6 7 CFD (which by composition corresponds to cement raw meals, i.e., non-calcined feed materials) acts mainly like a relatively inert diluent with its fine particles acting as fillers and 8 possibly serving as crystallization nuclei [10]. In contrast to CFD, CKD (which consists 9 predominantly of cement clinker materials) promotes the formation of hydration products and 10 hardening, and acts as an activator for latent GGBFS. 11

In general, the results in this study show that the direct replacement of GGBFS by CKDs is 12 more effective than the direct recycling of dust with cement raw materials in kiln. CKD 13 utilized as an activator for latent GGBFS in the production of environmentally efficient 14 blastfurnace cements favours efforts towards sustainable development in cement and concrete 15 industry. Moreover, a study on the technical and environmental assessment of the 16 development and production of CEM III/A, B, C blastfurnace cements, as described in this 17 work, confirmed their cost-effective production due to lower required amounts of cement 18 clinker and energy, which at the same time conserves natural resources and reduces CO₂ 19 emissions, when compared to Portland composite cement, which in addition to 65 mass % 20 cement clinker, contains calcareous fly ash (the EN 197-1 cement type CEM II/B-W, the 21 standard strength classes 32.5N and 42.5N) [15]. 22

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- 25

1 4 Conclusions

2

The obtained results for chemical and physical as well as mechanical properties of all three 3 types of blastfurnace cements (CEM III/A, B, C), which have been presented in this study, 4 provide evidence that the CKDs (cement clinker dust or cement filter dust), collected from 5 different sources during the production of Portland cement, can be directly and effectively 6 used as a replacement for GGBFS. With the appropriate mix composition, i.e., the clinker-to-7 GGBFS ratio, the addition of CKDs can provide satisfactory overall performance regarding 8 chemical requirements, setting time, volume stability, and mechanical properties. Although 9 the addition of GGBFS results in lower strength at early ages, the replacement of Portland 10 cement clinker by GGBFS up to 72 mass %, does not have any negative effect on the 11 compressive strength of concrete after 28 days. Summarizing these experimental results the 12 13 following conclusions are proposed:

When comparing the average values of loss on ignition (1.81 mass %), insoluble
 residue (0.0024 mass %), sulphate content as SO₃ (2.92 mass %), alkali content as
 Na₂O-equivalent (0.40 mass %), and chloride content (0.0014–0.0042 mass %),
 obtained in all 27 BFSC blends (CEM III/A, B, C), with the EN 197-1 limited values
 (in mass %): 5.0, 0.5, 4.0, between 1.0 and 2.0, and 0.1, respectively, the values
 obtained meet the chemical requirements for cements. Moreover, the prepared CEM
 III/A, B, C blends exhibit much lower values then those specified by the standard.

The production of blastfurnace cements CEM III/A, B, C standard strength Class
 42.5N in accordance with the EN 197-1 requirements is possible for 16 of 27 blends
 prepared. All 9 CEM III/A blends and 7 CEM III/B blends meet the requirements, and
 no sample of CEM III/C meets the EN 197-1 requirements for the standard
 compressive strength Class 42.5N.

1	3. The strength development of CEM III/A, B, C blends was significantly affected by the
2	CKDs addition. As expected, the presence of the cement clinker dust as an activator
3	for latent GGBFS was more effective than the cement filter dust which acts as a filler
4	due to its low hydraulic reactivity.
_	
5	4. The direct replacement of GGBFS by CKDs in the production of economical and
6	environmentally efficient blastfurnace cement favours efforts towards sustainable
7	development in cement and concrete industry.
8	
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<u>TABLES:</u>

Table 1 Composition of blastfurnace cements (BFSC) [1]

Types of	Clinker	GGBFS	Minor additional
BFSC	(mass %)	(mass %)	constituents (mass %)
CEM III/A	35–64	36–65	0–5
CEM III/B	20-34	66–80	0–5
CEM III/C	5-19	81–95	0–5

Table 2 Chemical analysis of materials used (in mass %)

Materials	SiO ₂	Al_2O_3	Fe ₂ O ₃	CaO	MgO	SO_3	K ₂ O
	くくく						
Portland cement clinker	20.88	5.79	3.61	66.24	1.08	0.56	0.54
Gypsum	4.81	1.83	1.51	32.08	1.63	36.14	0.46
Granulated blastfurnace slag	40.51	9.86	0.94	37.75	7.73	0.26	1.22
Cement clinker dust, CKD	22.60	4.41	2.91	66.66	0.95	0.70	0.47
Cement filter dust, CFD	15.82	4.06	2.01	43.21	0.64	0.78	0.57

- 1 Table 3 Mixture proportions of control, ordinary Portland cement (OPC), CEM I 42.5N, and
- 2 blastfurnace cement, CEM III/A 42.5N, in mass %

Samples	Portland cement clinker	Granulated blastfurnace slag	Gypsum	Cement kiln dust	Cement filter dust
OPC	96.00	-	4.00	-	
U1	35.00	61.00	4.00	-	-
U2	57.00	39.00	4.00		-
U3	46.00	50.00	4.00	-	-
U4	35.00	57.00	4.00	4.00	-
U5	57.00	35.00	4.00	4.00	-
U6	46.00	46.00	4.00	4.00	-
U7	35.00	57.00	4.00	-	4.00
U8	57.00	35.00	4.00	-	4.00
U9	46.00	46.00	4.00	-	4.00

Table 4 Mixture proportions of blastfurnace cement, CEM III/B 42.5N, in mass %

Samples	Portland cement clinker	Granulated blastfurnace slag	Gypsum	Cement kiln dust	Cement filter dust
U10	20.00	76.00	4.00	-	-
U11	28.00	68.00	4.00	-	-
U12	24.00	72.00	4.00	-	-
U13	20.00	72.00	4.00	4.00	-
U14	28.00	64.00	4.00	4.00	-
U15	24.00	68.00	4.00	4.00	-
U16	20.00	72.00	4.00	-	4.00
U17	28.00	64.00	4.00	-	4.00
U18	24.00	68.00	4.00	-	4.00

2 Table 5 Mixture proportions of blastfurnace cement, CEM III/C 42.5N, in mass %

Samples	Portland cement clinker	Granulated blastfurnace slag	Gypsum	Cement kiln dust	Cement filter dust
_					A
U19	5.00	91.00	4.00	-	-
U20	14.00	82.00	4.00	-	-
U21	10.0	86.00	4.00		-
U22	5.00	87.00	4.00	4.00	-
U23	14.00	78.00	4.00	4.00	-
U24	10.00	82.00	4.00	4.00	-
U25	5.00	87.00	4.00	-	4.00
U26	14.00	78.00	4.00	-	4.00
U27	10.00	82.00	4.00	-	4.00

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Table 6 Chemical composition of control, ordinary Portland cement (OPC), CEM I 42.5N, and three types of prepared blastfurnace cements CEM III/A, B, C (where samples designated as U1 ... U9, U10 ... U18, and U19 ... U27 denote CEM III/A, CEM III/B and CEM III/C, respectively), in mass %

Samples	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na_2O^2	IR ³	Cl
OPC	4.87	19.62	5.16	3.41	62.63	1.17	2.07	0.38	0.39	0.0100
CEM III/A										
U1	1.56	31.43	6.31	2.60	49.64	4.50	2.87	0.39	-	-
U2	1.97	27.88	5.85	2.98	53.85	3.60	2.74	0.42	-	-
U3	1.44	29.72	6.05	2.83	52.07	3.98	2.81	0.40	0.36	0.0028
U4	0.45	31.28	6.13	2.72	51.04	4.37	2.92	0.40	-	-
U5	0.76	27.16	5.83	3.11	56.30	3.09	2.66	0.40	-	-
U6	2.64	28.58	5.92	2.85	52.58	3.57	2.76	0.40	0.38	0.0021
U7	3.08	30.83	5.99	2.51	49.31	4.27	2.92	0.39	-	-
U8	4.05	26.54	5.70	2.83	54.05	3.09	2.63	0.41	-	-
U9	2.72	28.88	5.94	2.69	52.11	3.71	2.84	0.41	1.01	0.0031
CEM III/B										
U10	0.42	34.71	6.58	2.29	46.44	5.37	3.09	0.41	-	-
U11	0.31	33.26	6.46	2.56	48.33	4.97	3.00	0.41	-	-
U12	1.83	33.41	6.40	2.41	46.67	5.09	3.08	0.40	0.40	0.0017
U13	1.89	33.51	6.39	2.32	46.63	5.14	3.05	0.38	-	-
U14	2.10	32.00	6.19	2.53	48.41	4.65	3.01	0.40	-	-
U15	1.62	32.91	6.31	2.48	47.71	4.85	3.04	0.39	0.51	0.0021
U16	2.61	33.50	6.35	2.17	46.03	5.20	3.04	0.40	-	-
U17	2.81	32.05	6.23	2.37	47.67	4.76	3.01	0.40	-	-
U18	2.86	32.80	6.21	2.25	46.66	4.97	3.16	0.40	0.99	0.0042
CEM III/C										
U19	1.19	37.47	6.78	2.07	42.36	6.28	2.76	0.40	-	-

U20	1.01	35.78	6.58	2.33	44.54	5.69	2.97	0.40	-	-
U21	1.11	36.58	6.65	2.12	43.66	6.01	2.77	0.41	0.49	0.0014
U22	0.80	36.91	6.70	2.11	43.50	6.03	2.86	0.39	-	-
U23	0.29	35.35	6.48	2.35	45.86	5.55	3.02	0.40	-	-
U24	1.80	35.56	6.43	2.15	44.35	5.71	2.94	0.38	0.42	0.0017
U25	2.53	36.41	6.64	1.85	42.49	6.08	2.92	0.39	-	
U26	3.08	35.40	6.39	1.84	43.81	5.46	2.85	0.43		-
U27	1.92	36.71	6.62	1.89	42.84	5.79	3.08	0.44	0.94	0.0027

¹Loss of ignition, ²Na₂O-equivalent, ³Insoluble residue

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<u>FIGURES</u>:



Figure 1 XRD plots of materials used in this study: GGBFS (black plot), filter dust (blue plot), Portland cement clinker (red plot), and clinker kiln dust (green plot) [15].



Figure 2 Water required for standard consistency for all analysed cement blends.



Figure 3 Initial and final setting times for all analysed cement blends.





Figure 4(a) Compressive strength development of control CEM I cement mortar and U1-U9 (CEM III/A) cement mortar blends.



Figure 4(b) Compressive strength development of control CEM I cement mortar and U10-U18 (CEM III/B) cement mortar blends.



Figure 4(c) Compressive strength development of control CEM I cement mortar and U19-U27 (CEM III/C) cement mortar blends.



Figure 5(a) Flexural strength development of control CEM I cement mortar and U1-U9 (CEM III/A) cement mortar blends.



Figure 5(b) Flexural strength development of control CEM I cement mortar and U10-U18 (CEM III/B) cement mortar blends.



Figure 5(c) Flexural strength development of control CEM I cement mortar and U19-U27 (CEM III/C) cement mortar blends.