INVESTIGATION OF THE POSSIBILITY OF ENVIRONMENTALLY FRIENDLY PORTLAND-COMPOSITE CEMENT CEM II/C-M (W+LL) PRODUCTION IN THE KAKANJ CEMENT PLANT

Nevzet Merdić[1], Nedžad Haračić[1], Ilhan Bušatlić[2], Nadira Bušatlić[2], Adnan Mujkanović[2], Nedžib Kobilica[3]

[1]Cement Plant Kakanj, Bosnia and Herzegovina
[2]University of Zenica, Bosnia and Herzegovina
[3]Prevent Visoko d.o.o., Bosnia and Hezegovina

Keywords: Clinker, fly ash, limestone, compressive strength, setting time,

ABSTRACT
Public demand for environmentally friendly solutions for new types of cement with reduced CO_2 emissions is increasing. Consequently, new types of cement must be developed and introduced to the market. This paper presents test results for cement formulations based on calcium fly ash and marly limestone, following the EN 197-5 standard. The clinker content was set at 50% and 60%, with fly ash content at 25% and 35%, while marly limestone content remained fixed at 11%. Due to the use of marly limestone, which lacks pozzolanic properties, the cements were ground to a higher specific surface area to enhance their physical-mechanical properties. The test results show that these cement formulations meet the EN 197-1 standard requirements for specific cement classes.

1. INTRODUCTION

The European standard EN 197-5 defines Portland-composite cement with clinker additions ranging from 36% to 50%. The content of limestone that can be used in Portland-composite cements ranges from 6 to 20% (Table 1). The calcium carbonate ($CaCO_3$) content, calculated from the calcium oxide content, shall be at least 40% by mass, and the combined content of calcium carbonate and magnesium carbonate ($CaCO_3$ and $MgCO_3$), calculated from the calcium oxide and magnesium oxide content, respectively, shall be at least 75% by mass [1]. According to the EN 197-1[2] standard, the clay content, determined by the methylene blue test in accordance with EN 933-9 [3], shall not exceed 1,2 g/100 g. For this test, the limestone shall be ground to a fineness of approximately 5000 cm^2/g, determined as specific surface in accordance with EN 196-6 [4]. Additionally, the total organic carbon (TOC) content, when tested in accordance with EN 13639, shall conform to one of the following criteria [5]:

- LL: shall not exceed 0,20 % by mass,
- L: shall not exceed 0,50 % by mass.

In general, there are three mechanisms by which limestone can modify the properties of Portland cement:

- $CaCO_3$ participates in the reaction with C_3A (tricalcium aluminate) forming the monocarboaluminate phase. This phase is stable and coexists with the monosulfate phase which is the "normal" product of the reaction between gypsum and C_3A. Otherwise, the formation of the carboaluminate phase usually occurs later due to the disappearance or reduction of ettringite (the initial product of the reaction between C_3A and sulfate),
- Influences the increase in the rate of hydration of the C_3S (tricalcium silicate) phase,
- It affects the distribution of particles in the cement paste and thereby improves the optimization of its standard consistency, reduces water separation and segregation. Additionally, since limestone is ground with clinker and is generally softer than clinker, it will tend to grind finer than clinker. The fineness of the grain size increases the reactivity of $CaCO_3$ and improves the packing of particles in the prepared cement [6]. For the mentioned tests, limestone from the Ribnica quarry was used.

Acording to the EN 197-1, calcareous fly ash is a fine powder, having hydraulic and/or pozzolanic properties. It consists essentialy of reactive CaO, Reactive SiO_2 ad Al_2O_3. The remainder contains iron oxide (Fe_2O_3) and other components. The proportion of reactive calcium oxide shall not be less than 10,0% by mass. Calcareous fly ash containing between 10,0% and 15,0% by mass of reactive calcium oxide shall contain not less then 25,0% by mass of reactive silicon dioxide. The calcareous fly ash used in this tests is obtained as a by-product of coal combustion at the Kakanj thermal power plant.

Common grinding of fly ash and clinker results in a change in granulometry, so that porous agglomerates in fly ash tend to disperse and large particles are crushed. This co-grinding increases the reactivity of fly ash by increasing the specific surface area and uniforming the particle size of both fly ash and cement [7]. The composition of Portland-ement CEM II/C-M is specified in table 1.

Table 1. Portland-composite cement CEM II/C-M [1].

<table>
<tr><td rowspan="4">Main types</td><td colspan="2" rowspan="3">Notation of the products (types of cement))</td><td colspan="11">Composition (percentage by mass[a])</td></tr>
<tr><td colspan="10">Main constituents</td><td rowspan="3">Minor additional constituents</td></tr>
<tr><td>Clinker</td><td>Blast furnace slag</td><td>Silica fume</td><td>Pozzolana: natural</td><td>Pozzolana: Natural calcined</td><td>Fly ash: siliceous</td><td>Fly ash: calcareous</td><td>Burnt shale</td><td colspan="2">Limestone</td></tr>
<tr><td>Type name</td><td>Type notation</td><td>K</td><td>S</td><td>D[b]</td><td>P</td><td>Q</td><td>V</td><td>W</td><td>T</td><td>L[c]</td><td>LL[c]</td></tr>
<tr><td>CEM II</td><td>Portland-composite cement [d]</td><td>CEM II/C-M</td><td>50-64</td><td colspan="9">←---------------------36-50--------------- →</td><td>0-5</td></tr>
</table>

a The values in the table refer to the sumo f the main and minor additional constituents
b In case of the use of silica fume, the proportion of silica fume is limited to 6-10 % by mass
c In case of the use of limestone, the proportion of limestone (sumo f L, LL) is limited to 6-20 % by mass
d The number of main constituents other than clinker is limited to twoo and these main constituents shall be declared by designation of the cement (for examples, see Clause 6).

2. EXPERIMENTAL

2.1. Materials

Standard clinker (Kakanj plant), fly ash (Power plant Kakanj), limestone (Ribnica quarry) and raw gypsum (Bistrica deposit near Gornji Vakuf) were used for the experimental part of this work. Table 2 shows the chemical analyzes of the components used, which were performed on an XRF spectrometer. The chemical composition of the components was determined using a Bruker S8 Tiger spectrometer. Table 3 shows the mineralogical analyzes performed on a diffractometer. Mineralogical composition was determined on a Bruker D8 Endeavor device. In order for clinker, fly ash and limestone to be used for the production of cement, certain requirements must be met according to the European standard EN 197 – 1. Table 4 shows the requirements of the EN 197-1 standard, as well as the obtained test results for the components used [2].

Table 2. Chemical composition of clinker, fly ash, limestone and gypsum

Component (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Chloride
Clinker	22,18	5,36	3,12	66,94	0,98	0,65	0,03	0,51	0,005
Fly ash	40,28	17,42	7,94	25,03	2,11	2,07	0,27	1,46	0,001
Limestone	10,12	0,89	0,68	48,30	0,30	0,07	0,00	0,08	
Gypsum	4,99	1,53	0,64	33,56	3,14	42,11	0,03	0,43	

Table 3. Mineralogical composition of clinker, fly ash and limestone

Minerals	Clinker (%)	Fly ash (%)	Limestone (%)
Alit (C_3S)	61,56	3,86	
C_2S	18,43	11,85	
C_3A	5,25		
C_4AF	10,41		
Free CaO	1,04	2,50	
Periclase (MgO)	0,13	0,41	
Quartz (SiO_2)	0,06	3,44	9,68
Arcanite (K_2SO_4)	1,03		
Portlandite ($Ca(OH)_2$)	0,04	0,26	
Amorphous phase		63,41	
Calcit		1,25	85,12
Mullite		4,65	
Magnetite		1,53	
Hematite		1,60	
Thenardite		2,33	
Rutile		0,98	
Kaolinite			1,19

Table 4. Requirements of EN 197-1 and results for clinker, fly ash and limestone [2]

	Requirements EN 197-1 (%)	Clinker (%)	Fly ash (%)	Limestone (%)
$C_3S + C_2S$	≥66,6	79,99		
CaO/SiO_2	>2,0	3,01		
MgO	<5,0	0,98		
Reactive CaO (EN 197-1, point 3.1)	≥10		21,08	
Reactive SiO_2(EN 197-1, point 3.2)	>25		39,64	
$CaCO_3+MgCO_3$	>75			86,90
Clay content				0,10
TOC				0,06

2.2. Mix proportion and preparation

For the preparation of each sample, 3 kg of samples (clinker, fly ash, limestone and gypsum) were weighed in a certain percentage according to table 5. For these tests, the clinker content according to EN 197-1 was taken in the amount of 50% (U1) and 60% (U2). The sample thus weighed was ground in a laboratory ball mill until the required specific surface area was reached. After that, the standard consistency and setting time were determined (according to standard EN 196-3 [8], as well as the preparation of standard cement prisms of dimensions 4x4x16 cm for flexural and compressive strength testing according to standard EN 196-1 [9].

Tabela 5. Mix proportion of components

Type cement according to EN 197-5	Clinker (%)	Fly ash (%)	Limestone (%)	Gypsum (%)
CEM II/C-M (W+LL)	50	35	11	4
CEM II/C-M (W+LL)	60	25	11	4

3. RESULTS AND DISCUSION

Table 6 shows the chemistry of portland-composite cements examined in this paper, while table 7 shows the physical and mechanical properties of these cements examined in this paper. Table 8 shows the requirements of the EN 197-1 standard for the physical-mechanical properties of cement.

Table 6. Chemical composition of portland-composite cements

Sample	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O
U1	27,77	10,25	4,87	44,79	1,40	3,06	0,21	1,02
U2	25,08	8,79	4,28	49,96	1,28	3,11	0,16	0,91

Table 7. Physical and mechanical properties of cements

	R 009 (%)	Specific surface (cm^2/g)	Stand.conz. (%)	Setting time		Compressive strength (MPa, days)					
						Flexural			Compressive		
				Initial (min.)	Final (min.)	2	7	28	2	7	28
U1	0,1	5180	24,6	120	190	2,7	4,4	7,5	13,5	23,5	42,3
U2	0,1	4960	24,4	105	170	3,5	5,3	7,6	18,0	29,1	47,2

Table 8. Requirements of EN 197-1 for physical-mechanical properties of cement [2]

Strength class	Compressive strength (MPa, days)				Initial setting time (min)	Soundness (mm)
	Early strength		Standard strength			
	2 days	7 days	28 days			
32,5 N	-	≥ 16,0	≥ 32,5	≤ 52,5	≥ 75	≤10
32,5 R	≥ 10,0	-				
42,5 N	≥ 10,0	-	≥ 42,5	≤ 62,5	≥ 60	
42,5 R	≥ 20,0	-				
52,5 N	≥ 20,0	-	≥ 52,5	-	≥ 45	
52,5 R	≥ 30,0	-				

In this examination, clinker meets all the requirements of the European standard EN 197-1. Regarding fly ash, reactive CaO and reactive SiO2 also meet European standard EN 197-1 (reactive Cao is 21,08% and reactive SiO_2 is 39,64%. Also, limestone satisfying acoording standard EN 197-1 in terms of sum $CaCO_3$ and $MgCO_3$ (86,90%). The total content of CaO, SiO_2 and MgO in granulated blast furnace slag according to the EN 197-1 standard must be greater than 66,6%, and the granulated blast furnace slag used for these tests has a content of these components of 85,21%. The standard consistency both of cement samples is very similar and ranges from 24,40% to 24,60%. The setting times of the cement samples meet the requirements of the standard according to table 6.

Regarding the compressive strength results, both of samples have compressive strength values after 2 days greater than 10 MPa (13,5 MPa and 18,0 MPa) and they meet the requirements of the EN standard 197-1. Also, after 7 days both of cements satisfied requirements according to standard EN 197-1. After 28 days, all samples meet the requirements of the EN 197-1 standard in terms of compressive strength and they have values 42,3 MPa and 47,2 MPa.

4. CONCLUSIONS

Since the test results show that both samples meet certain requirements of the EN 197-1 standard, then these samples could be assigned the corresponding cement label. Thus, for sample U1, the mark could be CEM II/B-M (W+LL) 32,5N, while sample U2 could have the mark CEM II/B – M (W+LL) 42,5N. Both cements meet the requirements of the standard, both for early compressive strength and for late compressive strength. It is important to note that sample U1 could easily meet the requirements of the EN 197-1 standard for cement class CEM II/B – M (W+LL) 42,5N by increasing the specific surface area of that sample or slightly increasing the clinker content. If the specific surface area in sample U1 were to be increased, then the reactivity of the sample would also increase, so that sample could easily have a higher compressive strength after 28 days and could satisfy a higher cement class. Of course, this requires additional testing.

5. REFERENCES

[1] EN 197-5:2022, Cement - Part 5: Portland-composite cement CEM II/C-M and composite cement CEM VI

[2] EN 197-1:2019, Cement - Composition, specifications and conformity criteria for common cements

[3] EN 933-9:1998, Test for geometrical properties of aggregates-Part 9: assessment of fines – Methylen blue test

[4] EN 196-6:2000, Metode ispitivanja cementa-Dio 6:Određivanje finoće mliva

[5] EN 13639:2002, Determination of total organic carbon content in limestone

[6] N. Merdić, Ispitivanja mogućnosti proizvodnje portland cementa sa dodatkom laporovitog krečnjaka kao pucolanske komponente uzimajući u obzir parametre propisane standardima za cement, Magistarski rad, Zenica, 2008.

[7] N. Merdić, Razvoj nove klase portland-kompozitnih cemenata u Tvornici cementa Kakanj, Doktorska disertacija, Zenica, 2015.

[8] EN 196-3:2019, Metode ispitivanja cementa-Dio 3: Određivanje vremena vezivanja i stalnosti zapremine

[9] EN 196-1:2019, Metode ispitivanja cementa-Dio 1: Određivanje čvrstoće cementa