Mineralogical and chemical composition of the mineral admixtures which use Serbian cement factories

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The most of the cements production in Serbia, approximately 95 per cent, are standardized blended Portland cements based on Portland cement clinker mixed with mineral admixtures such as granulated blast furnace slag, natural and industrial pozzolana, limestone and gypsum. The aim of investigation were to determines mineral and chemical composition of the mineral admixtures which domestic cement factories uses in their regular production as their quality can great contribute to the quality of the cements produced.

Key words*: cement, mineral admixtures, composition*

1. INTRODUCTION

As we step into the 21st century and Portland cement crosses 175 years of age, the rising global cement consumption touches 1,500 million ton mark. Although there has been a significant change in the strength characteristics of cement since Aspin era, the cement industry is faced with several new challenges in this millennium. One of these is the impact of the Kyoto agreement to reduce atmospheric CO_2 emission. Production of binary, ternary and quaternary components blended cements appears to be a viable solution to achieve environmental target. Another advantages for blended cements production is cost savings.

The properties of some blended cements were studied from the end of the past century, however their world-wide diffusion is more recent. Their general behaviors is quite similar to that of Portland cement since they generally contain remarkable percentages of Portland cement clinker and, when hydrating, give the same calcium silicate and aluminates hydrates.

Blended cements are currently divided into three main families:

- Cements containing blast furnace slag
- Cements containing pozzolanic materials (natural and industrial) and
- Cements containing limestone.

Pozzolanic and blast furnace slag cements complying with special specifications, such as low heat development, high chemical resistance, prevention of expansion due to the alkali-silica reaction, are classified also among special cements.

For a long period Serbian cement factories use granulated blast furnace slag, natural and industrial pozzolana as a mineral admixture for production of Portland cement. Blast furnace slag used in Serbian cement factories are by-product obtained by smelting iron ore in ”Smederevo”; natural pozzolana – tuff is from ”Vranjska banja” while the coal ashes is delivered from different thermal power plants sited in Jagodina, Svilajnac, Vreoci and Lučani.

During 1997. Institute for testing of materials, together with all tree Serbian cement factories, started work on the program “Production cements conformed with requirements given in the standard JUS EN 197-1[1]. Our previous results[2] has shown that mineral admixtures which uses domestic cement factories in their regular production satisfies specific criteria’s proposed by standard JUS EN 197-1. Mineral admixtures which use Lafarge - Beočin cement factory, a.d.., and Titan cement factory “Kosjerić” in their regular production of Portland cement are enumerated in Table 1.

In this work we present results of mineralogical and chemical analysis of the mineral admixtures given in the Table 1. The chemical analysis were performed according prEN 196-2.2[3], which is an reference analytical method utilizing

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X-ray fluorescence, thus alternative method for the cements testing (alternative to the JUS EN 196-2.1[4]) but which can also be applied to the cement constituent materials.

Table 1 - Mineral admixtures which uses domestic cement factories in their regular production (users and their origin)

Mineral admixture	***User***	***Origin-notation***
Blast furnace slag (S)	Lafarge - Beočin cement factory	Smederevo I –**S1**
		Radinac – **S2**
	Titan Cement factory "Kosjerić"	Smederevo II – **S3**
Limestone (L)	Lafarge - Beočin cement factory	Srednje brdo – L1
		Mutalj – **L2**
	Titan Cement factory "Kosjerić"	Godljevo - **L3**
Gypsum – calcium sulfate	Lafarge - Beočin cement factory	Zorka-Subotica I - **G1**
	Titan Cement factory "Kosjerić"	Zorka-Subotica II – **G2**
Industrial pozzolana (Q)	Lafarge - Beočin cement factory	Banja Koviljača – **Q1**
		Loznica – **Q2**
		Kragujevac I – **Q3**
	Titan Cement factory "Kosjerić"	Kragujevac II – **Q4**
Natural pozzolana (P)	Titan Cement factory "Kosjerić"	Tuff-Vranjska banja – **P1**

2. EXPERIMENTAL

Examined mineral admixtures are enumerated in the Table 1.

Analytical techniques

Mineralogical analysis were performed by X-ray diffractometer HZG-4/C CARL ZEISS-JENA by follow working conditions:

X-ray	CuKα
Anticathode	Cu
Anode voltage	40 kV
Current intensity	20 mA
Filtration	Ni
Brans length	1.54Å
Rate	1^{O} 2θ/min
Registration	Scintillatic
Detector voltage	1700
Goniometer	horizontal

Chemical analisis were performed by X-ray fluorescence spectrofotometer ARL – 8480 – S SEQ – SIM – XRF) by follow working conditions:

Anticathode	Rh
Crystall selectors	Li, Ge, Tl (2d-2.85Å, 1.8Å, 6.53Å i 25.8Å)
Anode voltage	60 kV, 40 kV i 30 kV
Current intensity	40 mA, 60 mA i 80 mA

It is important to notiffy that anticathode is selected according material.

3. RESULTS AND DISCUSSION

Mineralogical composition

Determination of mineralogical composition is not obvious and included in testing according standards for cements and its constituents but it is important for assessing quality of applied raw materials.

The obtained mineralogical composition of the blast furnace slag, limestone, gypsum, natural and industrial pozzolanas is presented in Tables 2-6, respectively.

Table 2 - Glass content in blast furnace slag expressed in % by mass and amorphous share

Mineral component	S1	S2	S3
Melilite	47.37	36.84	42.86
Larnite-senonite g.	26.32	20.18	33.33
Brownmillerite	13.16	11.40	11.90
$Ca_3Fe_2Si_3O_{12}$(+/-Al)	6.58	31.58	7.14
Calcite	6.57	-	4.77
Amorphous share	75	64	73

Blast furnace slag from Smederevo in comparation with slag from Radinac have increased amorphous share, increased concentration of melilite and decreased concentration in calcium-ferro-silicates and alumino-silicates.

Table 3 - Glass content in limestone expressed in % by mass

Mineral com.	L1	L2	L3
Calcite	87.91	95.56	89.64
Quartz	9.07	-	6.44
Hematite	1.65	-	1.12
Dolomite	1.37	2.39	2.80
Seracite	-	1.37	-
Chlorite	-	0.68	-

Limestone from Srednje brdo is to very good raw material for cement industry due high calcite and law dolomite concentration. This limestone is poor silificated, it has significant quantity of quartz which has negative influence on crushing process.

Limestone from Mutalj is a very good raw material for cement production due to high calcite and law dolomite concentration.

Limestone from Godljevo is poor silicated limestone and it is relatively appropriate as a raw material for cement production although it contains high calcite concentration.

Table 4 - Glass content in gypsum expressed in % by mass

Mineral com.	G1	G2
Gypsum	94.74	83.07
Qartz	5.26	-
Bassanite	-	10.54
Chlorite	-	6.39

Gypsum from Zorka-Subotica I have a high gypsum content. As impurity, it contains only quartz, about 5 % by mass.

Natural pozzolana - tuff due to law quartz concentration may be regarded, by its origin, as an andezite tuff.

Table 5 - Glass content in natural pozzolana - tuff expressed in % by mass and amorphous share

Mineral com.	Tuff
Chlorite	3.72
Quartz	33.92
Gypsum	2.19
Feldspar	37.20
Liskunes	15.32
Amfiboles	4.81
Epidotes	2.84
Amorphous share	22

Examined industrial pozzolanas are coal ashes (mixtures of fly ashes and bottom ashes) from Serbian thermal power plants. The mineralogical composition of the coal ashes differs from sample to sample due:

- Differences in minerals and phases contained in coal and having undergone no phase transition (silicates, oxides, volcanic glass, coal particles)
- Differences in phases formed during burning (magnetite, hematite, metakaolinite, mullite, anhydrite, lime, periclase, Ca-Mg silicates, glass, semicoke, coke)
- Differences in minerals and phases formed during the transport and storage of fly ashes and bottom ashes (sulphates, carbonates and oxyhydroxides)

Table 6. Glass content in industrial pozzolanas expressed in % by mass and amorphous share

Min.com.	Q1	Q2	Q3	Q4
Quartz	67.98	22.95	28.62	8.66
Felspar	9.85	9.82	8.62	-
Calcite	7.39	36.89	25.86	36.80
Haematite	5.42	5.74	3.45	3.90
Amfiboles	3.94	-	2.08	3.90
Gypsum	3.45	9.02	7.93	24.24
Magnetite	1.97	4.10	1.72	1.73
Liskunes	-	11.48	-	-
Dolomite	-	-	11.03	-
Chlorite	-	-	4.48	2.16
Tridimite	-	-	4.14	-
Sericite	-	-	2.07	2.60
Pyroxene	-	-	-	5.19
Cristobalite	-	-	-	4.33
Portlandite	-	-	-	3.46
CaO free	-	-	-	3.03
Am. share	49	34	34	43

Chemical composition

Blast furnace slag, limestone, gypsum, natural and industrial pozzolanas chemical composition are given in Tables 7-11, respectively. Chemical analysis were performed using X-ray fluorescence spectroscopy, as it being increasingly employed, particularly where large numbers of cement analysis are required, including cement works control.

Table 7 - Blastfurnace slags chemical composition in % by mass (< 2e means that concentration is less than 2x Std.Err.)

Comp	S1	S2	S3
SiO_2	33.7±	32.6±0.2	33.7±0.2
Al_2O_3	11.2±0.2	11.0±0.2	11.2±0.2
Fe_2O_3	0.57±0.03	0.97±0.04	0.67±0.03
CaO	40.5±0.2	43.7±0.2	41.1±0.2
MgO	7.9±0.1	8.2±0.1	8.1±0.1
SO_3	<2e	<2e	<2e
S	0.49±0.03	0.52±0.03	0.51±0.03
Na_2O	0.58±0.03	0.66±0.03	0.53±0.03
K_2O	0.74±0.04	0.75±0.04	0.72±0.04
MnO	0.84±0.04	0.68±0.03	0.69±0.03

It is well known that blast furnace slag chemical composition can vary over a vide range depending on the nature of the ore, the composition of the limestone flux, the coke consumption and the kind of iron being made. It can also change over the years with alteration in sources of ore being smelted. Those variations affect the relative content of the major and minor components.

Table 8 - Limestone chemical composition in % by mass (<means that concentration is less than 10 ppm,< 2e means that concentration is less than 2x Std.Err.)

Comp	L1	L2	L3
Na_2O	0.058±	0.049±0.07	0.049±0.07
MgO	0.44±0.03	0.41±0.02	0.40±0.02
Al_2O_3	2.19±0.07	0.33±0.02	1.86±0.06
SiO_2	9.0±0.1	0.80±0.04	5.0±0.1
S	<2e	<	<2e
SO_3	0.032±0.003	0.23±0.02	0.032±0.003
K_2O	0.35±0.02	0.040±0.003	0.21±0.01
CaO	43.1±0.2	55.9±0.2	47.8±0.2
MnO	0.048±0.004	0.0043±0.006	0.0106±0.001
Fe_2O_3	0.63±0.03	0.124±0.009	0.62±0.03

Blast furnace slag has quite the same chemical composition and their quality is appropriate for use in cement industry [5].

Limestone can be used as a filler when its proportion in cement not exceeds 5 % by mass. In that case there are no quality requirements for it. When limestone applies as a mineral admixture it shall meet some requirement: carbonate content must exceed 75 % by mass and content of clay and organic matter. All limestone meets cited requirements.

Table 9 - Gypsum chemical composition in % by mass (< means that concentration is less than 10 ppm,)

Comp	**G1**	**G2**
Na_2O	0.079±0.007	0.080±0.007
MgO	0.024±0.003	0.043±0.004
Al_2O_3	0.26±0.02	0.14±0.01
SiO_2	2.17±0.07	0.71±0.04
S	<	<
SO_3	39.6±0.2	40.8±0.2
K_2O	0.019±0.002	0.061±0.005
CaO	35.6±0.2	34.2±0.2
MnO	<	0.0020±0.0006
Fe_2O_3	0.16±0.01	0.21±0.01

Gypsum from Zorka-Subotica, although by-product in phosphorous – acid production, is a quality raw material which is important when considering overall Portland cement quality.

Table 10 - Natural pozzolanas chemical composition in % by mass (< means that concentration is less than 10 ppm)

Comp	**Tuff**
Na_2O	1.80±0.06
MgO	1.67±0.06
Al_2O_3	17.7±0.2
SiO_2	58.1±0.2
S	<
SO_3	1.81±0.06
K_2O	3.94±0.09
CaO	2.00±0.07
MnO	0.086±0.007
Fe_2O_3	4.46±0.10

According to tuff chemical composition, primarily to its silica concentration which is about 60 % by mass, this tuff might be also classified as a decite tuff.

Table 11 - Industrial pozzolana chemical composition in % by mass (< means that concentration is less than 10 ppm)

Comp	Q1	Q2	Q3	Q4	Coal (siliceous fly ash)	Lignite (calcareous fly ash)
Na_2O	0.33±0.02	0.45±0.03	0.29±0.02	0.96±0.04	0.2-2	-
MgO	2.22±0.07	2.59±0.08	2.07±0.07	4.04±0.10	-	
Al_2O_3	27.1±0.2	16.3±0.2	21.6±0.2	8.3±0.1	28-35	12-15
SiO_2	52.5±0.2	37.0±0.2	40.9±0.2	25.7±0.2	47-54	18-25
S	0.046±0.012	<	<	<	-	-
SO_3	0.033±0.02	4.18±0.10	3.38±0.09	10.5±0.2	0-1	5-9
K_2O	1.70±0.06	1.24±0.05	1.96±0.06	0.76±0.04	1-6	-
CaO	8.2±0.1	28.4±0.2	21.6±0.2	41.4±0.2	1-2.5	2-3
MnO	0.085±0.007	0.080±0.006	0.085±0.007	0.18±0.01	-	-
Fe_2O_3	5.90.1±0.1	8.4±0.1	6.6±0.1	7.0±0.1	4-12	6-8

According to chemical composition examined coal ashes are difficult to classify especially as they are mixtures of fly ashes and bottom ashes.

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REZIME

MINERALOŠKI I HEMIJSKI SASTAV MINERALNIH DODATAKA KOJE KORISTE FABRIKE CEMENTA U SRBIJI

Najveći deo proizvodnje cementa u Srbiji, približno 95%, su standardizovani mešani cementi na bazi Portland cementnog klinkera kome se dodaju mineralni dodaci: granulisana zgura visoke peći, prirodni i industrijski pucolani, krečnjak i gips. Cilj ispitivanja je bio da se odredi mineraloški i hemijski sastav mineralnih dodataka koje domaće fabrike cementa koriste u svojoj redovnoj proizvodnji, jer oni mogu značajno doprineti kvalitetu i osobinama proizvedenih cemenata.

Ključne reči: *cement, mineralni dodaci, sastav*