

THE EFFECT OF ASH RESULTED IN WOOD-BASED PANNELS MANUFACTURING PROCESS ON THE PROPERTIES OF PORTLAND CEMENT

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In this study, was assessed the influence on the hydration and hardening processes of partial substitution of Portland cement with an ash (CK) resulted in the burning of wood waste, in the wood-based panels manufacturing process. This ash has a high amount of calcium carbonate and quartz and is a very fine material – average particle size smaller than 30 microns.

For this study, mixtures of Portland cement with various amount of CK ash (5% up to 20%) were prepared and tested. The analyses performed on cement pastes showed an increase of water for normal consistency and setting time when the amount of CK ash increase in binder's compositions.

The higher compressive strengths were achieved when Portland cement is substituted with 10% CK ash.

Keywords: ash; Portland cement; properties, hydration and hardening processes

1. Introduction

Portland cement industry uses by-products from other industries, such as blast furnace slag, coal ash, pyrite ash, silica fume, etc. [1-9], or combustible wastes, such as used tires, petroleum oils, etc. [10-13]. These by-products or wastes, depending on their compositional characteristics, are used in different stages of the Portland cement manufacturing process i.e. burning of raw mix for clinker production or grinding of the clinker with gypsum and other additions.

Coal ash is a by-product resulting in the combustion of coal in power plants to produce electricity and it is used in cement factories as a grinding addition to the of Portland clinker [14]. According to the literature data [6, 7, 15-23] the substitution of clinker with coal ash (fly ash) leads to the decrease of the mechanical strength of Portland cement at early ages (up to 28 days), but will contribute to the increase of the durability of hardened cement stone.

In this study a different type of ash was used to partially substitute (5% up to 20%) the cement in the production of CEM II cements. This ash (CK) results in the wood-based panels manufacturing process, by the burning of wood residues in

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order to produce heat. The temperature in the heat generator, in which take place the burning of wood waste, is lower (around 800°C) than the temperature achieved in thermal power plant boiler (over 1100°C). CK ash is recuperated from the dedusting system of gas.

In this paper are presented results regarding the influence of the partial substitution of Portland cement with CK ash on the hardening processes and properties of the resulted cements.

2. Materials and methods

2.1. Materials

The oxide composition of fly ash (CK), was obtained by X-ray fluorescence spectrometry (Table 1). It can be observed that the main oxides are silica (SiO_2), calcium oxide (CaO) and alumina (Al_2O_3); also, it can be noticed a high content in alkaline oxides ($\text{K}_2\text{O} + \text{Na}_2\text{O} = 7.38\%$). Because CK was obtained from a deposit it is moist, therefore it was dried at 50°C for 48 hours and then homogenized in a ball mill for 30 minutes.

Table 1

Oxide composition of CK			
Oxide composition	(%)	Oxide composition	(%)
SiO_2	41.63	P_2O_5	1.3
Al_2O_3	8.64	TiO_2	0.65
Fe_2O_3	4.83	Mn_2O_3	0.87
CaO	22.44	Cl	0
MgO	2.98	S	0.49
SO_3	1.23	C	2.44
K_2O	6.06	Moisture	3.53
Na_2O	1.32	Loss of ignition.	7.5

The Portland cement (CP) used was of type CEM I 52.5 R, with a Blaine specific area of 4102 cm^2/g , determined according to SR EN 196-6, Part 6 [24]; the oxide and mineralogical composition of CP are given in the Table 2.

The quantitative mineralogical composition of CP was estimated by Rietveld analysis.

2.2. Methods

The oxide composition was assessed by X-ray fluorescence spectrometry. The mineralogical composition was assessed by X-ray diffraction (XRD) coupled with Rietveld analysis; XRD analyses were performed in the range $2\theta = 5\text{--}65$ degrees, using a Shimadzu XRD 6000 ($\lambda = 1.5406\text{ \AA}$) and PANalytical Cubix ($\lambda = 1.5418\text{ \AA}$);

The microstructure of CK ash and hardened cement mortars was assessed by scanning electron microscopy (SEM) by means of Quanta Inspect F scanning electron microscope (1.2 nm resolution) coupled with EDX.

The cement hydration and hardening processes were assessed on pastes with water to binder ratio of 0.5, hardened for 1 up to 90 days. The water for normal consistency and setting times of cements were determined according to European and corresponding Romanian standard norm SR EN 196-3-2017 [25].

Table 2
Oxide and mineralogical composition of Portland cement

Oxide (%)	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	LOI
	20.58	5.22	2.68	64.97	1.27	3.61	0.78	0.58	5.75
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Minera-logic (%)	C ₃ S (Alite)	C ₂ S (Belite)		C ₃ A cubic	ortho-hedric	Total	C ₄ AF (Ferrite)		
	66.34	11.08		4.01	2.88	6.89	8.67		

Compressive strength was assessed on mortar specimens prepared according to SR EN 196-1, Part 1 [26], using as aggregate polygranular sand; the binder:aggregate ratio was 1: 3 and water:binder ratio was 0.5. The mortar specimens were cast in cuboid molds (15x15x60mm), vibrated for 2 minutes and cured for 1 up to 28 days in humid air (R.H. 90%). The compressive strengths were assessed with a Matest machine, and the final values represent the mean of at least four strength values assessed on specimens cured in similar conditions with a deviation of $\pm 10\%$ [26].

3. Results and discussion

3.1. Characterisation of raw materials

The X-ray diffraction analysis performed on CK – Fig. 1, showed the presence of the following main crystalline mineralogical phases: mullite (Al₂O₃·2SiO₂·3Al₂Si₂O₁₃); quartz (SiO₂); calcite (CaCO₃); calcium aluminium silicate (Ca₃Al₂Si₂O₁₀).

From the morphological point of view, the SEM images presented in Fig.2, show ash particles with a predominantly spherical morphology (including the cenospheres and plerospheres), with the average size smaller than 30 μm .

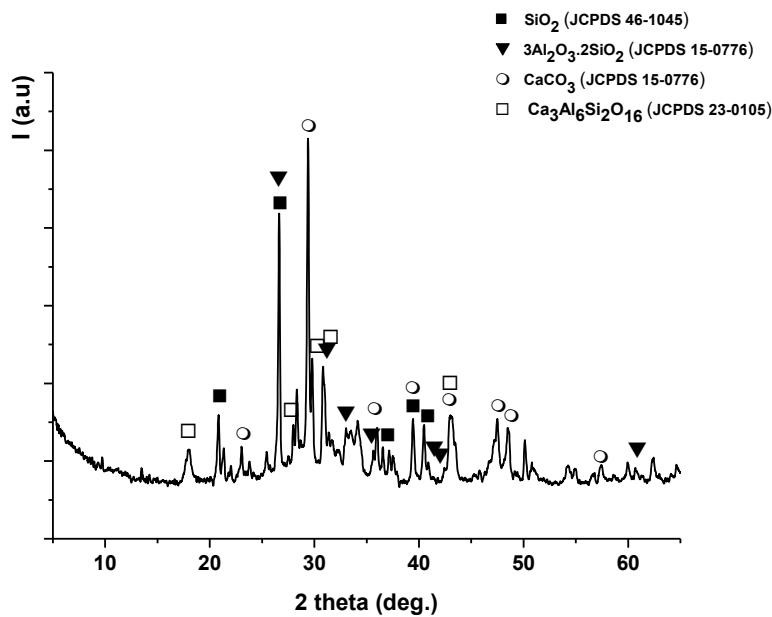


Fig.1. X-ray diffraction patterns of CK ash

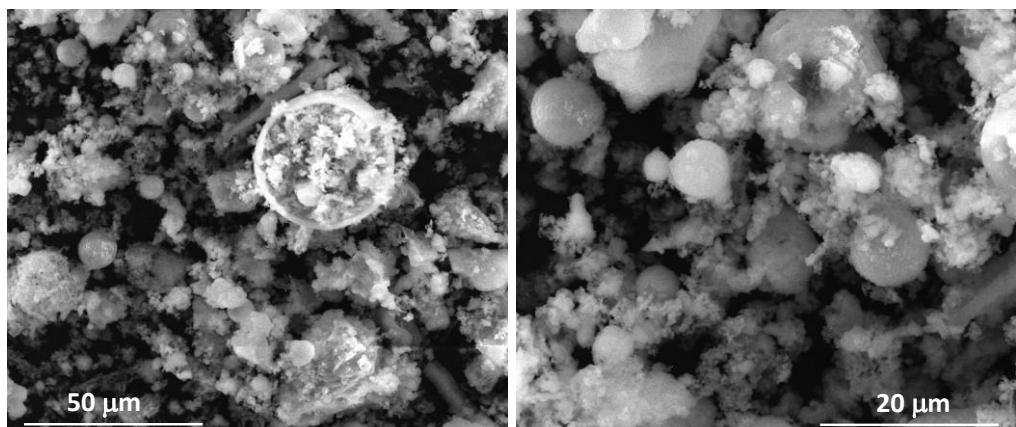


Fig.2. Scanning electron microscopy images of CK ash

Fig. 3 shows the X-ray diffraction patterns of Portland cement (CP). The mineralogical composition is correlated with the data presented in Table 2 and the main compounds assessed by this method are: calcium silicates (C_3S - Ca_3SiO_5 ; C_2S - Ca_2SiO_4); tricalcium aluminate (C_3A - $\text{Ca}_3\text{Al}_2\text{O}_6$) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

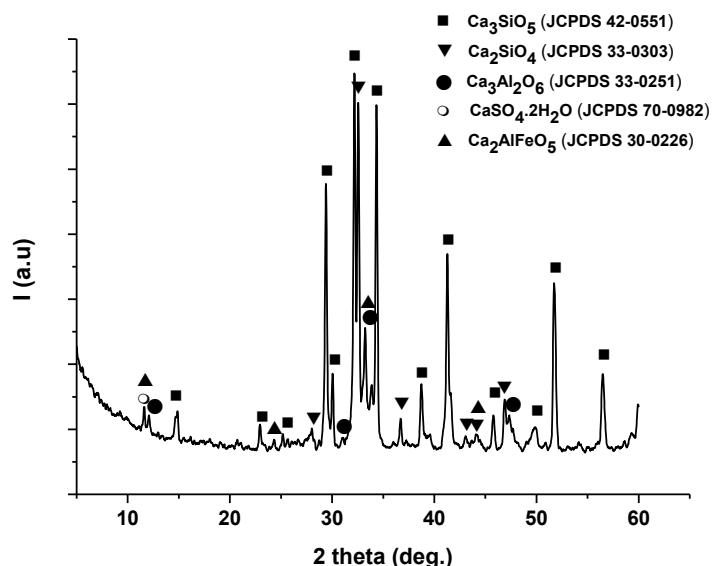


Fig.3. X-ray diffraction patterns of Portland cement (CP)

The compositions of binders obtained by the mixing of CP and CK are presented in Table 3; the degree of substitution of CP with CK was comprised between 0 and 20%.

Table 3

Composition of the studied binders		
Symbol	Cement (PC) (wt%)	CK ash (wt.%)
E	100	-
M1	95	5
M2	90	10
M3	85	15
M4	80	20

3.2. Properties of Portland cements with CK addition

The values of water for normal consistency and the setting times of cement pastes are presented in Table 4. One can observe that the values of water for normal consistency increases with the increase of CK amount, most probably due to the morphological characteristics of CK ash; CK is a very fine powder and can partially absorb the water added in the system.

The initial and final setting times increase with the increase of CK content in the binder composition. This can be explained by dilution of cement and water absorption capacity of CK ash.

Fig. 4 shows the variation of the compressive strengths vs. the curing time; for all studied binders the compressive strength increases with the increase of

curing time. Also, the content of CK ash in cement influences the value of the compressive strengths, as follows:

- at shorter curing times (one day), compressive strength decreases with the increase of CK content, most likely due to a delaying effect of the Portland cement hydration-hydrolysis processes;

- at longer curing times (one year), for a low content of CK ash (10-15%), the compressive strength increases with 24-31%, compared to the reference (E)-plain PC;

- The increase of CK content over 15% determines a decrease of compressive strengths most probably due to a higher degree of substitution of CP (with binding properties) with CK ash.

According to the data presented in Fig. 4 the higher compressive strengths were recorded for M2 therefore 10% substitution of CP with CK is considered optimal.

Table 4

Properties of studied binders

Binder symbol	Water for normal consistency (ml/100 g)	Setting time (min.)	
		Initial	Final
E	33.2	110	140
M1	33.6	220	398
M2	33.8	265	490
M3	34	272	500
M4	34.2	300	-

"-" - the final setting time was not determined, being longer than 500 min.

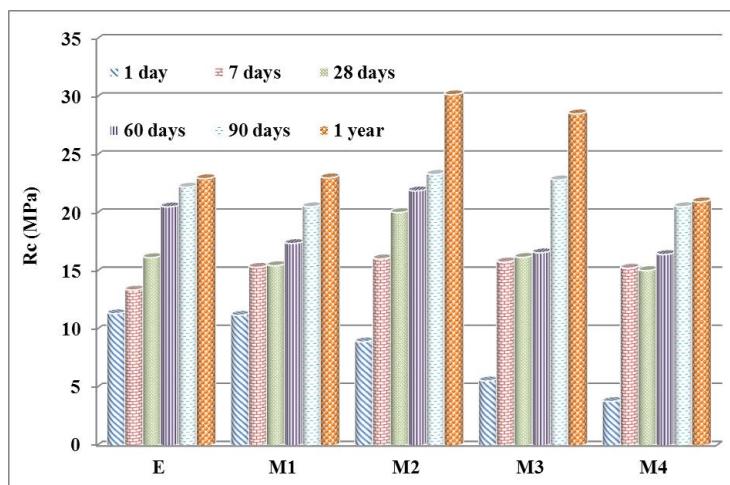
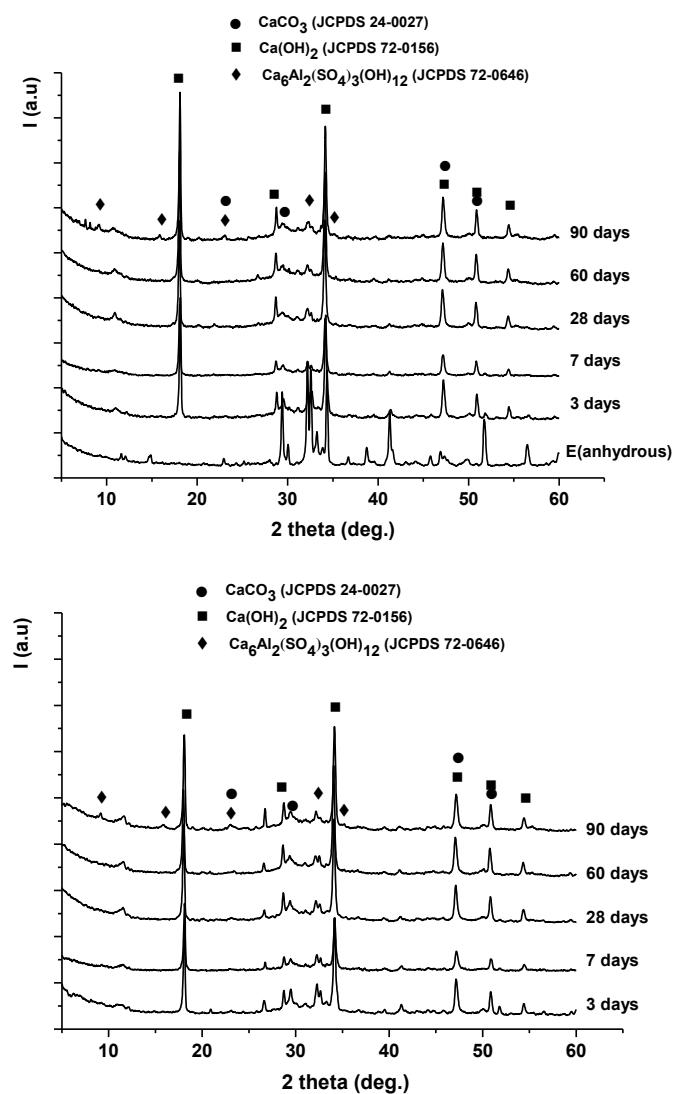


Fig.4. Compressive strengths vs. time

XRD patterns of cement pastes with/without CK ash, hardened at 3, 7, 28, 60 and 90 days, are presented in Fig. 5; one can assess the hydration of Portland

clinker by the reduction of XRD peaks specific for anhydrous compounds and the appearance of the diffraction peaks characteristic for the following hydrates: ettringite ($\text{Et-Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$) portlandite ($\text{CH-Ca}(\text{OH})_2$) and calcium carbonate (CaCO_3 - CaCO_3) resulted by the CH carbonatation with atmospheric CO_2 . Also, very low intensity interferences for calcium silicates hydrates (CSH; JCPDS 72-0156) and AFm-type phases formed at longer hardening times by ettringite transformation were highlighted.



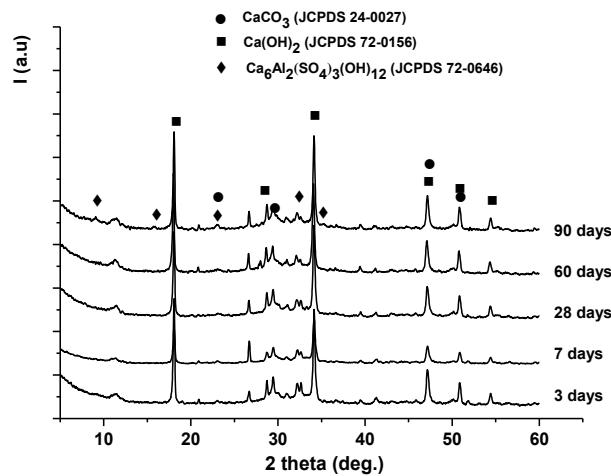
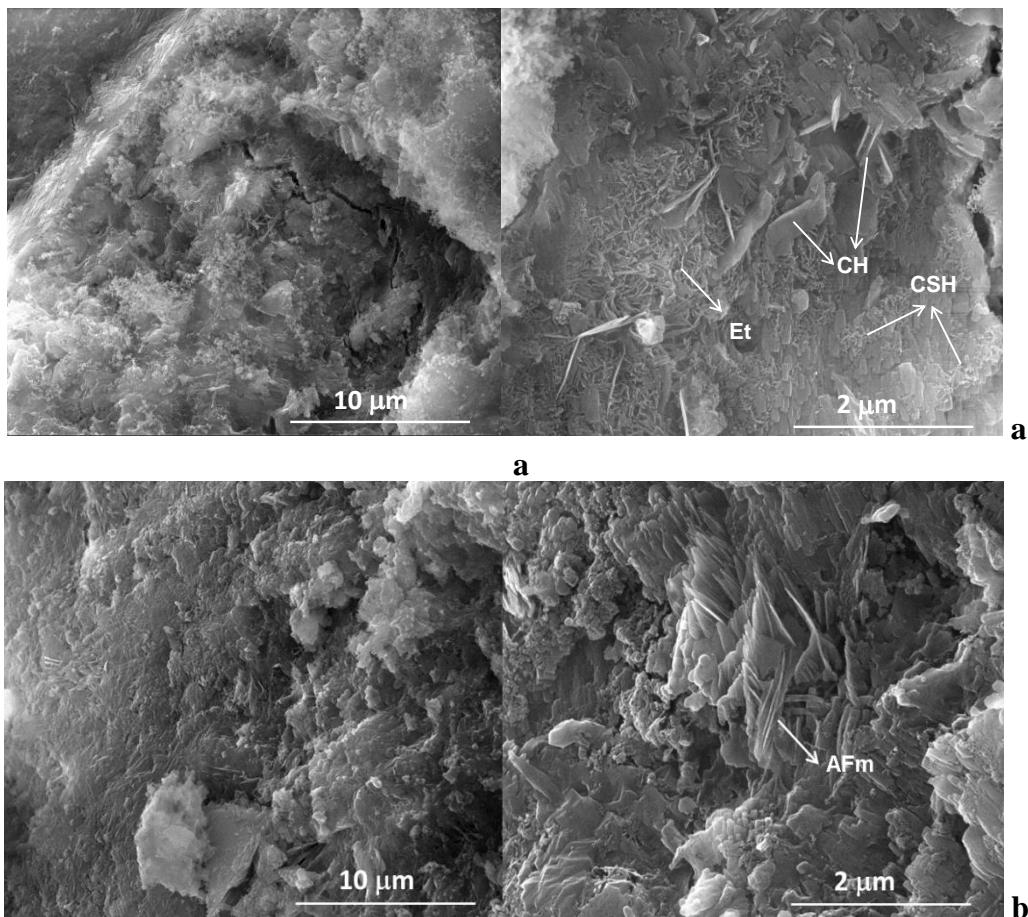


Fig.5. X-ray diffraction images for the binder mixtures hardened at different time periods: a- E; b- M2; c- M4.



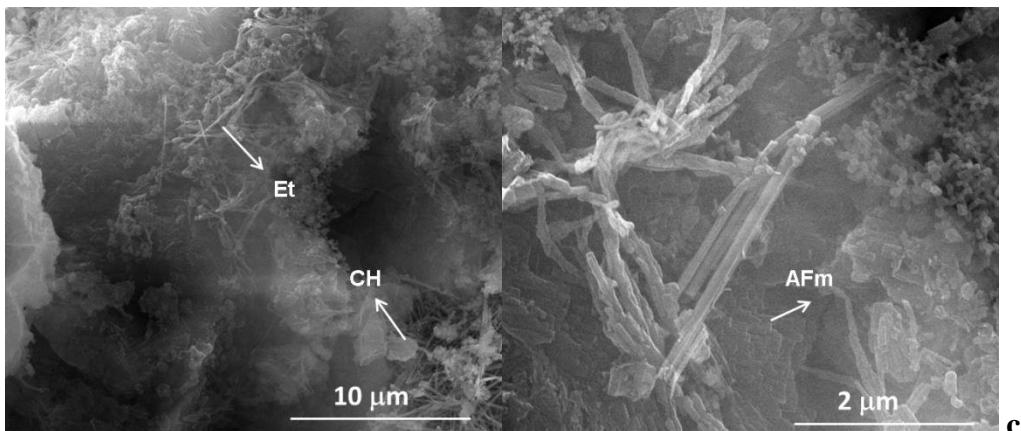


Fig.6. Scanning electron microscopy images on 28-day hardened mortars: a- E; b- M2; c- M4.

From a microstructural point of view, the SEM images – Fig. 6, show for all studied specimens, morphologies characteristic for hydrates [27]: hexagonal plates characteristic of the portlandite (CH); fine acicular formations and crinkled foils characteristic of calcium silicate hydrates (CSH); large acicular crystals characteristic of the ettringite (Et); thin hexagonal plates characteristic of the monosulfate phase (AFm).

4. Conclusions

CK ash (resulted by the burning of wood waste in the manufacture of wood-based panels) can be used to substitute various amounts of Portland cement, in order to obtain CEM II Portland cements. The analyses performed on cement pastes showed an increase of water for normal consistency and setting time when the amount of CK ash increase in binder's compositions. The higher compressive strengths were achieved when Portland cement is substituted with 10% CK ash. The nature of hydrates formed in the cement pastes with CK content is similar with those formed in ordinary Portland cement (CEM I).

R E F E R E N C E S

- [1]. *S.H. Kosmatka, B. Kerkhoff, W.C. Panarese, Design and control of concrete mixtures, Cap. 3- Fly Ash, Slag, Silica Fume, and Natural Pozzolans, pp. 57- 70, 14th. Edition, Portland Cement Association, 2008.*
- [2]. *K.Y. Show, Industrial Waste, A. Seco, F. Ramirez, L. Miquelez, P. Urmeneta, B. García, E. Prieto, V. Oroz- Cap.7 Types of waste for the production of pozzolanic materials – a review, pp. 141- 150, InTech, 2012.*
- [3]. *M. Panjehpour, A.A. Abang Ali, R. Demirboga, A review for characterization of silica fume and its effects on concrete properties, International Journal of Sustainable Construction Engineering & Technology , 2 (2), december, 2011*
- [4]. *A. Shyam, A. Anwar, S.A. Ahmad, A literature review on study of silica fume as partial replacement*

of cement in concrete, International Journal of Advanced Engineering, Management and Science, 3 (3), 250-253, 2017

- [5]. A. Imam, V. Kumar, V. Srivastava, Review study towards effect of Silica Fume on the fresh and hardened properties of concrete, Advances in Concrete Construction, 6 (2), 145-157, 2018.
- [6]. M. Ondova, A. Sicakova, Review of , trends in ways of fly ash application, 14th International Multidisciplinary Scientific GeoConference SGEM 2014, Conference Proceedings, June 19-25, Book 5, **Vol. 2**, 603-610, 2014.
- [7]. A.R.K. Gollakota, V. Volli, C.-M. Shu, Progressive utilisation prospects of coal fly ash: A review, Science of The Total Environment, 672, 951-989, 2019.
- [8]. E. Ozbay, M. Erdemir, H.I Durmus, Utilization and efficiency of ground granulated blast furnace slag on concrete properties – A review, Construction and Building Materials, 105, 423-434, 2016.
- [9]. E.K. Garg, E.K. Kapoor, A review on ground granulated blast-furnace slag as a cement replacing material, International Journal of Engineering Research and Management, 3 (7), 214-217, 2016.
- [10]. M. Manzanera, Alternative Fuel, **Cap. 11** M.P.M. Chinyama, Alternative fuels in cement manufacturing, pp. 263-284, InTech, 2011.
- [11]. A. Rahman, M.G. Rasul, M.M.K. Khan, S. Sharma, Impact of alternative fuels on the cement manufacturing plant performance: an overview, Procedia Engineering, 56, 393 - 400, 2013.
- [12]. M. Georgescu, G. Nicolae, Impact of the alternative fuels use on the composition and on the structural characteristics of the clinkers, Romanian Journal of Materials, 40(2), 102-111, 2010.
- [13]. C.(Gheorghe) Oproiu, G. Voicu, Effects of fuel type used for clinker burning on their characteristics, Romanian Journal of Materials, 45 (2), 133 – 137, 2015.
- [14]. SR EN 197-1-2011- Cement - Part 1: Composition, specifications and conformity criteria for common cements.
- [15]. W. Qadir, K. Ghafor, A. Mohammed, Characterizing and modeling the mechanical properties of the cement mortar modified with fly ash for various water-to-cement ratios and curing times, Advances in Civil Engineering, Article ID 7013908 (7 pp), 2019.
- [16]. Z. Giergiczny, Fly ash and slag, Cement and Concrete Research, 124, 105826, 2019.
- [17]. A. Yerramala and B. Desai, Influence of fly ash replacement on strength properties of cement mortar, International Journal of Engineering Science and Technology, 4 (8), 2012.
- [18]. H. Biricik and N. Sarier, Comparative study of the characteristics of nano silica-, silica fume and fly ash-incorporated cement mortars, Materials Research, 17 (3), 570 - 582, 2014.
- [19]. C. Jun, L. Gengying, Mechanical properties and drying shrinkage of self-compacting concrete containing fly ash, Romanian Journal of Materials, 46 (4), 480 - 484, 2016.
- [20]. M. Georgescu, N. Saca, Properties of blended cements with limestone filler and fly ash content, U.P.B. Sci. Bull., Series B, 71 (3), 2009.
- [21]. T. Yang, H. Zhu, Z. Zhang, X. Gao, C. Zhang, Q. Wu, Effect of fly ash microsphere on the rheology and microstructure of alkali-activated fly ash/slag pastes, Cement and Concrete Research, 109, 198–207, 2018.
- [22]. Y. Gao, C. Hu, Y. Zhang, Z. Li, J. Pan, Investigation on microstructure and microstructural elastic properties of mortar incorporating fly ash, Cement and Concrete Composites, 86, 315-321, 2018.
- [23]. X. Hu, C. Shi, Z. Shi, L. Zhang, Compressive strength, pore structure and chloride transport properties of alkali-activated slag/fly ash mortars, Cement and Concrete Composites, 104, Article 103392, November 2019.
- [24]. SR EN 196-6-2010, Methods of testing cement — Part 6: Determination of fineness.
- [25]. SR EN 196-3-2017, Methods of testing cement — Part 3: Determination of setting times and soundness.
- [26]. SR EN 196-1-2006, Methods of testing cement — Part 1: Determination of strength.
- [27]. D.H. Campbell, Microscopical examination and interpretation of Portland cement and clinker, second edition, Portland Cement Association, 1999.