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EFFECT OF ALTERNATIVE RAW MATERIALS OVER CLINCKER QUALITY AND CO_2 EMISSIONS

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Abstract: In the cement industry, the actual challenges are the preservation of the raw materials and energy resources, as well as reduction of pollutant emissions. In this context, the cement producers demand studies to reduce of the production costs and atmospheric emissions. One way to achieve these objectives, is to use alternative fuels or by-product raw materials. Any reduction in the required energy has a beneficial influence both on the viability of the cement plant and on the environment. One of the approaches aimed at reducing thermal energy consumption is the partial substitution of traditional raw materials (limestone, clay, gypsum) with other alternative materials, with a melting effect, among which stand out by-products of the steel industry such as furnace and steel slag. Another way for preservation of energy resources is using alternative fuels instead of traditional fuels like coal, petroleum coke or gas. The clinkering process and clinker quality can be influenced by any additions, in this study was determined these influences.

Keywords: *burning, clinker cement, emission, furnace slag, quality*

INTRODUCTION

The cement (OPC) is a construction material most used for housing and infrastructure [1]. About 3 $GJ \cdot ton^{-1}$ of clinker is used for OPC production, which accounts about 30 - 40 % of the total cost final product [2]. About 125 kg of coal 5 are consumed in the production of 1 tons of cement, while electricity consumption is around 95 - 125 $kWh \cdot ton^{-1}$ [3, 4]. In the European Union, around 25 million tons of coal are used for cement obtaining. In the cement industry, the main fuel used is coal, but an extensive range of different fuels such as petroleum coke, oils or tires wastes have been used successfully [5 – 8].
With 1.7 Gt of CO_2 emissions per year in 2022 - more than 8 % of global emissions from the burning of fossil fuels, therefore the main industrial sources of CO_2 emissions are the cement sector [9]. Different additives used in the cement fabrication lead to low energy consumption, other ways for reduction of CO_2 emission being the substitution of raw materials with different wastes, that are regarded as "carbon neutral", have as result the significantly decreasing in CO_2 emissions per ton of cement [10, 11]. Any decrease in the energy needed has a positive impact on the environment and the cement plant's sustainability [12].
In terms of quantity available and potential and actual areas of reuse, blast furnace slag is the most significant by-product of the steel industry [13]. It is resulting from the process of iron extracting from ores [14]. Blast furnace slag is formed because of the reduction reactions of iron oxides with carbon monoxide, originating from the burning of coke. In the furnace, along with iron ore and coke, limestone or dolomite is introduced to remove impurities (sulfur, phosphorus, silicon, aluminum, manganese etc.) through liquid phase reactions with calcium oxide. The melt formed, by the reaction of calcium oxide with iron ore impurities, separates as slag at the top, due to its much lower density 2200 $kg \cdot m^{-3}$ comparatively with molten iron 7800 $kg \cdot m^{-3}$.
In the metallurgical process, slags play an important role, because they ensure the complete separation of the metal from the ore. In addition, they have a loosening role by solubilizing cast iron impurities, especially sulphides [15].
The amount of resulting slag depends, to a large extent, on the performance of the process, the most efficient pig iron production processes can produce 250 - 300 kg of slag per ton of cast iron, and the average ratio of slag/cast iron is 0.8.
Granulated (GBS) and non-granular blast furnace slags (NGBS) are the two categories into which they are separated based on the cooling technique [16, 17]. The slags' chemical composition and rate of cooling influence their physical properties (density, porosity, and particle size) as well as their reactivity. The slag is a mixture of silicates, aluminates, and silico-aluminates of calcium, magnesium, and very small amounts of iron. This composition is a result of the metallurgical processes that occur in the furnace and the composition of the raw iron ore.
GBS is obtained by the rapid cooling of the slag melt in a stream of water or water with air, which leads to obtaining a granulated mass, which, on microscopic examination, shows glassy phase and crystalline components. The proportion of crystalline constituents depends on the cooling rate, the temperature at which the slag is evacuated from the furnace and the composition of them [18, 19]. GBS has latent hydraulic properties, that can be described by the ability to evolve slowly (especially in a basic environment) to a lower energy content, through hydrolysis reactions of calcium

silicates and aluminates. The progressive and continuous formation of hydro compounds has the effect of setting and hardening, with the development of mechanical resistances.

Ungranulated (crystallized) slag is obtained by slowly cooling the slag melt in air (at atmospheric conditions). The crystalline phases are mainly silicates and aluminosilicates of calcium and magnesium. The main crystalline phases are melilites, solid solutions with continuous isomorphism of gehlenite-akermanite-merwinite, and minor phases are wollastonite, dicalcium silicate, forsterite, anorthite and sulphides. They do not contain free MgO, and sulfides and colloidal iron give the slags reducing properties. Crystallized slag is characterized by chemical stability and hardness [20].

Actually, in the cement industry, GBS is used as a grinding additive to obtain: cement with slag, blast furnace cement and composite cements. The non-granular blast furnace slag can be used for: compact foundations from sorted slag aggregates for highways and airports, ballast for railway embankments, bituminous pavements, as a mineral aggregate, both for making bituminous mixes and macadam for construction and filter media for various fluids [21]. Steel slag is the by-product of making steel from cast iron, which is melted together with scrap iron, ferroalloys, fluxes in oxygen converters (BOF slag) and oxygen electric arc furnaces (EAF slag).

As novelty this study propose capitalization of different slags in mixtures of raw materials that is used in clikerization process, all determinations were realized in industrial furnace with a capacity of 3000 $t \cdot day^{-1}$.

MATERIALS AND METHODS

Materials characterization

The Galati furnace slag was used as alternative material. SEM, XRD, and EDS analyses were performed for the raw materials. X'Pert PRO MRD X–ray diffractometer – PANalytical (X–ray diffraction analysis – XRD) and SEM VEGA TESCAN Scanning Electron Microscope equipped with the QUANTAX Bruker EDS Microanalysis system were used for characterization**.**

Establishing the compositional recipes - making raw mixtures

To test the possibility of using furnace/steel slag as a raw material for the preparation of raw mixes for the manufacture of Portland cement clinkers, at the cement factory, a dosage of raw materials was considered that would lead to obtaining a clinker with modular characteristics and mineralogy comparable to those in current production.

The technological behavior of the furnace/steel slag in the raw mixture was reduced in comparison with a raw mixture, considered standard, obtained from current raw materials (limestone, marl, sand, pyrite ash).

The dosage calculations, presented in Table 1, were carried out based on the chemical composition of the raw materials considering the creation of raw mixtures with the following modular composition: Sk = 0.96; M_{Si} = 2.4; M_{Al} = 1.4. Raw mixtures of 4 and 5 components, as follows: for four components, Galati steel slag, without the

addition of Fe_2O_3 corrector from five components, using non-granulated blast furnace slag and granulated blast furnace slag.
The ratio of clay: slag was, 3:1 (mixtures TNG and TG1) and 1:1 (mixture TG2).
The raw mixtures were made by simultaneously grinding the raw materials, according to the dosage, until a fineness, expressed by the refusal on the 90 µm sieve of ~ 15 %. The proposed compositional recipes and the dosage of raw materials are presented in Table 1.

Table 1. *Dosage of raw materials*

Specification	**Raw mixtures**				
	E	**TOG**	**TNG**	**TG1**	**TG2**
Raw materials dosage [%]					
Limestone	75.76	74,65	74.5	74.1	72.2
Marl	18.32	17.96	14.2	15.0	11.0
Sand	4.8	4.88	5.0	4.5	4.1
Pyrite ash	1.12	-	1.4	1.4	1.7
Steel slag Galati	-	3.12	-	-	-
NGBS Galati	-	-	5.0	-	-
GBS	-	-	-	5.0	11.0

RESULTS AND DISCUSSION

Slag characterization

SEM Analysis

To establishing the possibilities to using the slag in cement production, it was characterized from point of view of morphological and physico-chemical properties. The size and shape of the particles are shown in Figure 1. Analyzing the data from Figure 1, the slag presented as a fine powder, with particles of various shapes and diameters. The slag has 75 % fine part, with particles below 5 µm. The existence of the coarse part demonstrates an open circuit grinding process. SEM micrographs of the form and surface texture of the GBS slag particles are displayed in Figure 2. The forms of the slag particles ranged from subrounded to subangular. Thick, subangular particles had clearly defined edges and asperities. The majority of the gravel-sized particles showed good sphericity and a robust structure. A few particles' surfaces also featured a heterogeneous porous structure.
The SEM analyses revealed that the slag had sand and silt sizes. Different asperities and edges were found in angular, bulky particles. The majority of particles with sand and silt sizes that were analyzed under the SEM exhibited rough surface textures. The data are in accord with literature [13, 20].

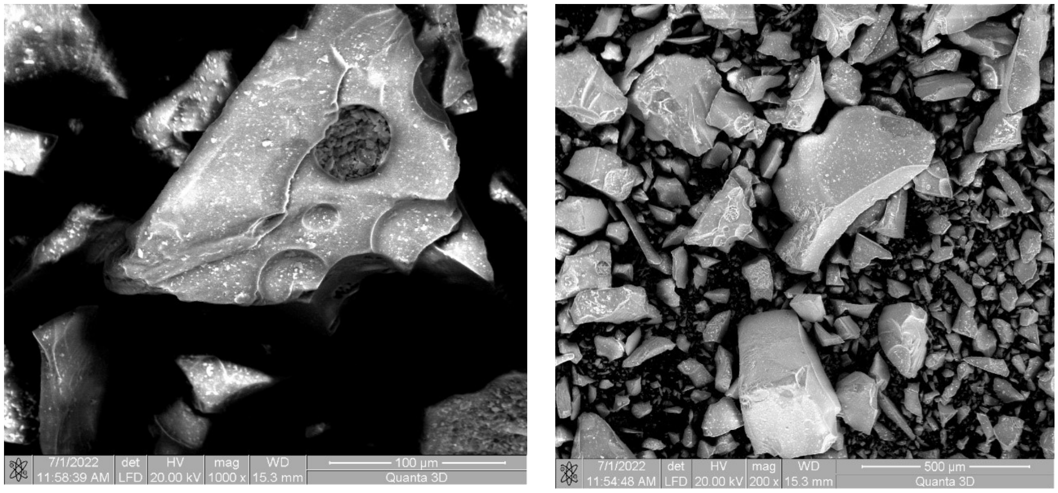

Figure 1. *The shape and dimensions of the BGS*

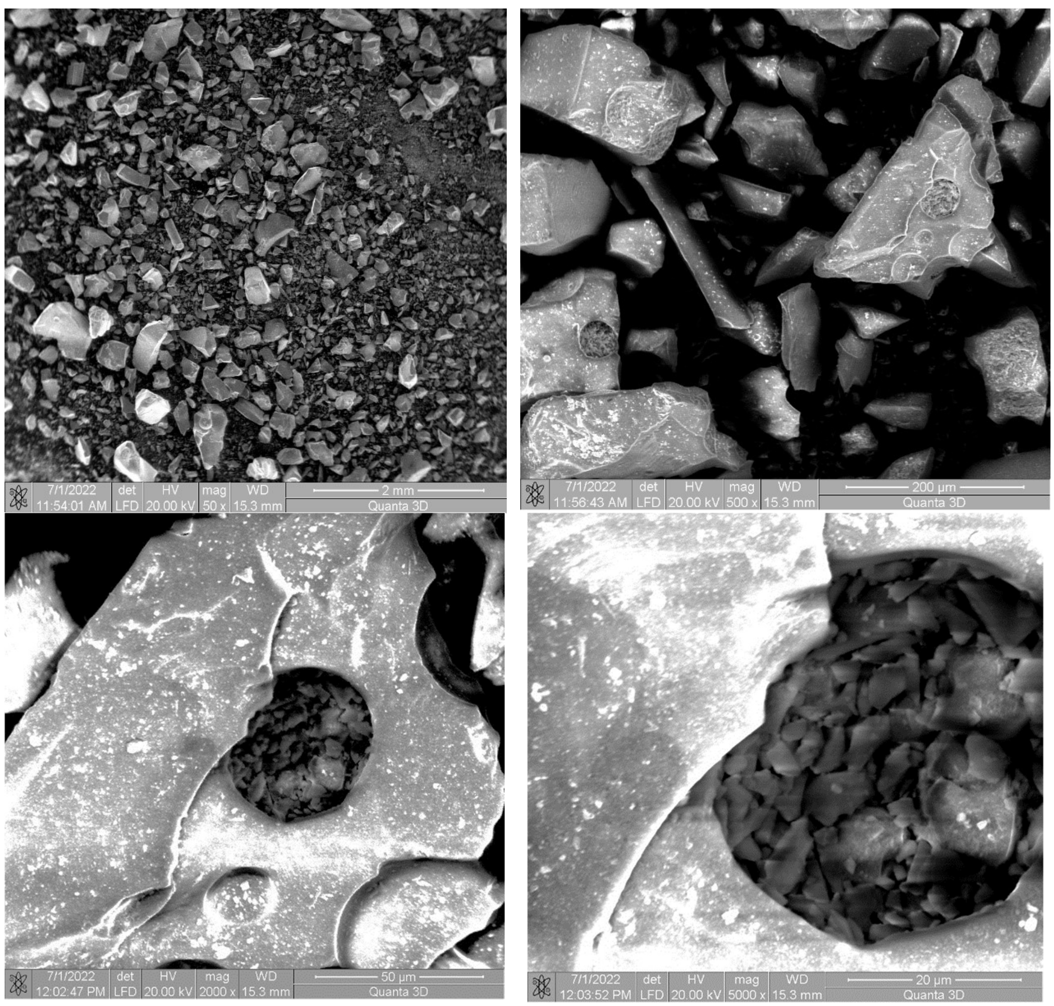

Figure 2. *The morphologic analysis of GBS*

Chemical composition

The composition of slag is variable, depending of type of slag and sources. Thus, the most common minerals are olivines, merwinites, C_2S, β-C_2S, C_4AF, C_2F, CaO-FeO-MgO and CaO solid solutions. Comparing the different blast furnace slags, notable quantitative differences are obtained, especially refer to content of ferric oxides, manganese oxide, presence of sulphur compounds etc. The important differences appear and in the SiO_2 and Al_2O_3 content, which is reflected in the physical-mechanical properties.

The composition of steel mill slag is close to that of Portland cement clinker. Table 2 present the chemical composition of different types of slag and Portland clinker.

Table 2. *Composition of some metallurgical slags and Portland cement clinker*

Composition, [%]	**Blast furnace slag**	**Steel mill slag (BOF)**	**Steel slag (EAF)**	**Clincher Portland**
SiO_2	35-39	11-18	8-18	18-25
Al_2O_3	8-12	1-4	3-8	3-8
Fe_{tot}	< 1	14-19	20-30	2-6
CaO	36-42	48-54	25-35	60-67
MgO	4-12	1-4	3-9	0-6
SO_3	2-3	< 0.5	< 0.5	1.5-4
TiO_2	0	0	0	0.21
Na_2O	0.3-0.6	0.12	< 0.1	0.19
K_2O	0.5-0.7	0.02	< 0.1	0.50

The obtained results for the chemical composition of NGBS are presented comparatively in Table 3.

Table 3. *The chemical composition of non-granulated slag from Galati*

Characteristic, [%]	**NGBS Galati**	
	sample 1	**sample 2**
SiO_2	36.49	36.53
Al_2O_3	9.42	10.71
Fe_2O_3	0.49	0.50
CaO	42.68	42.06
MgO	7.11	7.80
SO_3	1.30	0.20
Na_2O	0.18	0.64
K_2O	0.63	0.75

XRD analysis

The XRD analysis (Figure 3) demonstrates that the analyzed slag has a slightly crystallized structure, with positive effects on the concrete production process. Merwinite ($3CaO·MgO·2SiO_2$), olivine ($2MgO·2FeO·SiO_2$), α–C_2S and β–C_2S ($2CaO·SiO_2$), C_4AF ($4CaO·Al_2O_3·FeO_3$), C_2F ($2CaO·Fe_2O_3$), MgO, FeO, and C_3S ($3CaO·SiO_2$), and an uncrystallized, a solid solution of CaO–FeO–MnO–MgO, are frequent found in the slags. The diffractogram, Figure 3, indicates compounds of the calcium-aluminum-silicate type, in accordance with the specialized literature [13, 19, 22].

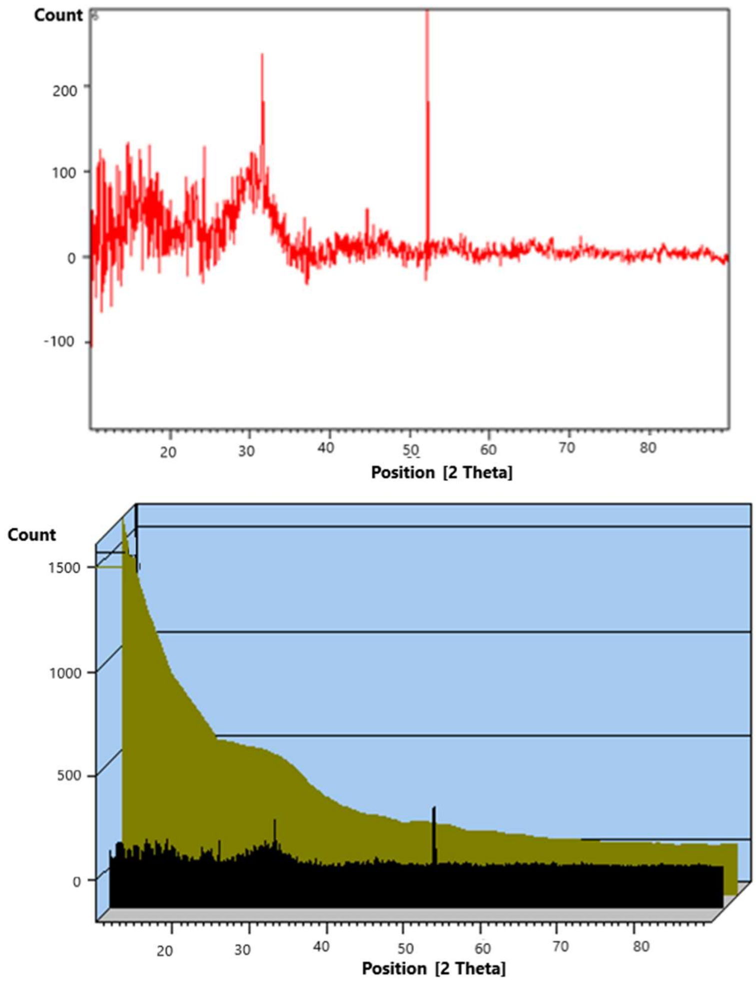

Figure 3. *XRD analysis for GBS*

Consideration about slag utilization over clinker quality

Based on the data presented in Table 1 and theoretical consumption of raw materials, table 4, the following considerations can be made, compared to the standard mixture of current raw materials:

- Galati steel slag can fully replace pyrite ash, reducing at the same time the proportion of limestone and marl with 1.5 %.
- the use of GBS and NGBS in a proportion of 5 % in the RM (TNG and TG1) determines the saving of limestone with 2 % of marl with 18 - 22 %, while the proportion of pyrite ash increased by 25 %.
- the use of NGBS determines increasing of sand with 4 %.
- GBS in content of 11 % in the flour reduced the raw materials with 40 % for marl, 5 % for limestone, and about 14 % of sand. GBS leads to an increase in the proportion of pyrite ash by approx. 50 %.

***Table 4**. Calculus of the theoretical consumption of raw materials [t·t^{-1} clinker]*

Raw materials	**Specific, theoretical consumption of raw materials [t·t^{-1} clinker]**				
	E	**TOG**	**TNG**	**TG1**	**TG2**
Limestone	1.16089	1.13398	1.12250	1.10597	1.06364
Marl	0.28072	0.27282	0.21395	0.22388	0.16205
Sand	0.07355	0.07413	0.07534	0.06716	0.06040
Pyrite ash	0.01716	-	0.02109	0.02090	0.02504
Steel slag Galati	-	0.04739	-	-	-
NGBS Galati	-	-	0.07534	-	-
GBS Galati	-	-	-	0.07463	0.16205

The calculated chemical and mineralogical composition of the flour of raw materials (RM), respectively of the clinkers (K) can be seen in Table 5.

***Table 5.** Characteristics of the clinker comparatively with raw materials composition*

	E		**TOG**		**TNG**		**TG1**		**TG2**	
	RM	**K**	**RM**	**K**	**RM**	**K**	**RM**	**K**	**RM**	**K**
Chemical composition [%]										
L.O.I*	34.74	-	34.2	-	33.6	-	33.55	-	32.12	
CaO	43.31	66.4	43.7	66.3	43.9	66.23	43.98	66.2	44.78	65.98
SiO_2	14.00	21.4	14.1	21.4	14.2	21.41	14.22	21.4	14.48	21.33
Al_2O_3	3.40	5.21	3.43	5.21	3.45	5.20	3.46	5.20	3.52	5.18
Fe_2O_3	2.43	3.72	2.45	3.72	2.47	3.72	2.47	3.71	2.51	3.70
MgO	0.68	1.05	0.78	1.18	0.97	1.46	1.00	1.50	1.38	2.03
Na_2O	0.46	0.70	0.46	0.69	0.43	0.65	0.43	0.65	0.41	0.60
K_2O	0.78	1.19	0.76	1.16	0.68	1.02	0.7	1.06	0.61	0.91
SO_3	0.20	0.3	0.17	0.26	0.20	0.30	0.19	0.29	0.19	0.27
Mineralogical composition [%]										
C_3S	-	66.71	-	66.67	-	66.57	-	66.53	-	66.32
C_2S	-	11.19	-	11.19	-	11.17	-	11.16	-	11.13
C_3A	-	7.53	-	7.52	-	7.51	-	7,51	-	7.48
C_4AF	-	11.33	-	11.33	-	11.3	-	11.3	-	11.27

**L.O.I. – Loss on ignition*

Analyzing the data from Table 5, it is clear that the chemical and technological behaviors of the Galati steel slags recommend these for using as a raw material, and the clinker and cement quality, that is produced, meeting the requirements of the SR EN 197-1 standard. This technological variant of making clinker, even if it requires a higher grinding energy consumption than in the case of the current raw mix, presents the following advantages: Furnace slag (non-granulated and granulated) can be used as a raw material in the flour mix, though, in order to obtain clinkers from the factory's usual compositional range, it is necessary that the mixture of raw materials consists of 5 components. The advantages of this technological variant, even if it requires additional energy consumption when grinding compared to the current raw mixture, are:
- reducing the proportion of limestone and marl in the mixture of raw materials;
- reduction of specific heat consumption by 0.20-0.47 GJ·t^{-1} clinker.

CONCLUSIONS

Decades of experience using waste as an alternative source of energy needed in the cement manufacturing process have demonstrated a solution that is ecologically justifiable. The use of slag as an alternative source of raw material represents an ecological solution and an efficient method of waste management.

Slag characterization demonstrated that it contains same components as clinker, but in other proportion. On the other hand, because the steel slag has suffered a thermal process, less fuel is required for combustion in the furnace, thus reducing CO_2 emissions from combustion. In addition, the calcium oxide in the slag replaces some of the limestone in the raw mix, which is another source of CO_2.

The all 4 mixtures analyzed at industrial scale, with the Galati steel slag, in flour mixture, demonstrated that slags can be used as raw materials, while the quality of the clinkers and cements obtained are in accord with the standard SR EN 197-1.

The solution of capitalization, analyzed in this paper, presents the following advantages: furnace slag (non-granulated and granulated) can be used as a raw material in the raw mix, however, in order to obtain clinkers from the factory's usual compositional range, it is necessary that the mixture of raw materials consists of 5 components. The advantages of this technological variant, even if it requires additional energy consumption when grinding compared to the current raw mixture, are: decreasing the proportion of limestone and marl in the RM and decrease of specific heat consumption by 0.20 - 0.47 $GJ \cdot t^{-1}$ clinker.

Taking into account the chemical and technological behaviors and the available quantities, both types of slag can be used at industrial scale with significant reduction of raw materials and CO_2 emissions.

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REFERENCES

1. Ige, O.E., Von Kallon, D.V., Desai, D.: Carbon emissions mitigation methods for cement industry using a systems dynamics model, *Clean Technology and Environment Policy*, **2024, 26**, 579-597, https://doi.org/10.1007/s10098-023-02683-0;
2. Gartner, E., Sui, T.: Alternative cement clinkers, *Cement and Concrete Research*, **2018**, **114**, 27-39;
3. Chatterjee, A.K.: Contemporary Cement Plants: Scale, Complexity, and Operational Variables: *In Intelligent and Sustainable Cement Production*, CRC Press, **2021**, 1-37;
4. Abdul-Wahab, S.A., Al-Dhamri, H., Ram, G., Chatterjee, V.P.: An overview of alternative raw materials used in cement and clinker manufacturing, *International Journal of Sustainable Engineering*, **2021**, **14** (4), 743-760;
5. Vasiliu, L., Gencel, O., Damian, I., Harja, M.: Capitalization of tires waste as derived fuel for sustainable cement production, *Sustainable Energy Technologies and Assessments*, **2023**, **56,** 103104;
6. Rahman, A., Rasul, M.G., Khan, M.M.K., Sharma, S.: Recent development on the uses of alternative fuels in cement manufacturing process, *Fuel*, **2015**, **145**, 84-99;

7. Schneider, M., Hoenig, V., Ruppert, J., Rickert, J.: The cement plant of tomorrow, *Cement and Concrete Research*, **2023**, **173**, 107290;
8. Beguedou, E., Narra, S., Afrakoma Armoo, E., Agboka, K., Damgou, M.K.: Alternative Fuels Substitution in Cement Industries for Improved Energy Efficiency and Sustainability, *Energies*, **2023**, **16** (8), 3533;
9. Sousa, V., Bogas, J.A., Real, S., Meireles, I.: Industrial production of recycled cement: Energy consumption and carbon dioxide emission estimation, *Environmental Science and Pollution Research*, **2023**, **30** (4), 8778-8789;
10. Vasiliu, L., Lazăr L., Harja M.: Reducing the carbon dioxide footprint of inorganic binders industry, *Journal of International Scientific Publications, Ecology & Safety*, **2023**, **17**, 35-43;
11. Cheng, D., Reiner, D.M., Yang, F., Cui, C., Meng, J., Shan, Y., Guan, D.: Projecting future carbon emissions from cement production in developing countries, *Nature Communications*, **2023**, **14** (1), 8213;
12. Vasiliu L., Lazar L., Fanache M., Harja M.: Analysing of possibilities to used of alternative fuels as energy sources, *Bulletin of the Polytechnic Institute of Iasi, Section of Chemistry and Chemical Engineering*, **2023**, **69** (4), 79;
13. Guo, Y., Luo, L., Liu, T., Hao, L., Li, Y., Liu, P., Zhu, T.: A review of low-carbon technologies and projects for the global cement industry, *Journal of Environmental Sciences*, **2024**, **136**, 682-697;
14. Fanache, M., Vasiliu, L., Harja, M.: Composite Materials with Glass Fiber Waste and Blast Furnace Slag, *Journal of Composites Science*, **2024**, **8** (7), 256;
15. Fang, K., Wang, D., Zhao, J., Zhang, M.: Utilization of ladle furnace slag as cement partial replacement: Influences on the hydration and hardening properties of cement, *Construction and Building Materials*, **2021**, **299**, 124265;
16. Li, Y., Liu, Y., Gong, X., Nie, Z., Cui, S., Wang, Z., Chen, W.: Environmental impact analysis of blast furnace slag applied to ordinary Portland cement production, *Journal of Cleaner Production*, **2016**, **120**, 221-230;
17. Guo, X., Shi, H.: Utilization of steel slag powder as a combined admixture with ground granulated blast-furnace slag in cement based materials, *Journal of Materials in Civil Engineering*, **2013**, **25** (12), 1990-1993;
18. Escalante, J.I., Gomez, L.Y., Johal, K.K., Mendoza, G., Mancha, H., Mendez, J.: Reactivity of blast-furnace slag in Portland cement blends hydrated under different conditions, *Cement and Concrete Research*, **2001**, **31** (10), 1403-1409;
19. Sun, J., Kong, K.H., Lye, C.Q., Quek, S.T.: Effect of ground granulated blast furnace slag on cement hydration and autogenous healing of concrete, *Construction and Building Materials*, **2022**, **315**, 125365;
20. Altun, I.A., Yılmaz, İ.: Study on steel furnace slags with high MgO as additive in Portland cement, *Cement and Concrete Research*, **2002**, **32** (8), 1247-1249;
21. Autelitano, F., Giuliani, F.: Electric arc furnace slags in cement-treated materials for road construction: Mechanical and durability properties, *Construction and Building Materials*, **2016**, **113**, 280-289;
22. Kumar, S., Kumar, R., Bandopadhyay, A., Alex, T.C., Kumar, B.R., Das, S.K., Mehrotra, S.P.: Mechanical activation of granulated blast furnace slag and its effect on the properties and structure of portland slag cement, *Cement and Concrete Composites*, **2008**, **30** (8), 679-685.