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Role of mineral additions in reducing CO_2 emission

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Abstract

The influence of the substitution of a part of clinker with the mineral additions, in the process of production of mixed cement, on mechanical characteristics of cement and the reduction of CO_2 emission is researched. Experiments are organized through the production of clinker, which has different phase structures, and cement, using different kinds and amount of mineral additions, with joint grinding and addition to the already ground cement. The most important of the effects analyzed, which include the reduction of thermal and electric energy, is the reduction of CO_2 emission.

Keywords: CO_2 emission; Cement; Clinker; Fly ash; Slag

1. Introduction

Current projections predict the increase of world population from present-day 6 billion to 9 billion in year 2050 to 11 billion by the end of the century [1]. Ensuring the basic demands for a population twice the size of the present-day population will considerably increase the pressure on water, food, land, river sources, energy, common goods, and services. In short, the world must be developed [1]. The universal aspiration of society for bigger progress should be adjusted to the capacities of the Earth to endorse that kind of development. Development needs considerable advances in basic knowledge, social capacity, and technologies to put into use what is already known.

Studies in the production of mixed cements that have been stimulated for increasing the quantity of produced cement and reduction of production expenses are already of historical significance [2]. Later research works have been oriented on finding the possibilities of improvement of characteristics during the modification of hydration systems [2,3].

The studies are being continued because of the need for sustainable development [1,4]. Approaches in the production of clinker for the purpose of the reduction of energy consumption and CO_2 emission are different and dependent on regional position of a factory (i.e., the disposability of natural and secondary raw materials, regulations of particular countries regarding environmental protection, etc.) [3,5–8].

The employment of alternative fuels (i.e., waste materials), which have exploitable energy, is in use for many years in the cement industry and it presents one way of conserving natural energy sources. Through this, thanks to the characteristics of clinker baking, waste materials are disposed of in a way that is safer for the environment. With that kind of approach, CO_2 emission, which would have been released by combustion at, e.g., an incinerating plant, is being reduced [9,10]. Three sources of CO_2 emission, which are the result of $CaCO_3$ decarbonization from raw material, the reaction of fuel combustion during the process of baking in rotary furnace and equivalent of electric energy consumption, are present in cement production [8,11].

One of the most significant activities today aims at a higher percentage of replacement of clinker in cement with secondary raw materials, with the possibility of improvement of cement characteristics and durability of concrete. With this kind of approach, the consumption of natural raw materials, thermal and electric energy, together with the reduction of CO_2 emission, are decreasing [1,6–10].

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Table 1
Parameters of clinker quality

Clinker	LSF in clinker (%)	Content of CaO in clinker (mass%)	Compressive strength—28 days (MPa)	CO_2 emission from decarbonization (kg/kg clinker)
1	99.1	65.3	59.7	0.513
2	96.5	64.0	57.3	0.502
3	93.2	63.4	51.5	0.498
4	92.0	63.0	48.5	0.495

Table 2
Gas combustion parameters

Clinker	Gas consumption (m^3/kg clinker)	CO_2 emission by gas combustion (kg/kg clinker)
1	0.102	0.198
2	0.100	0.194
3	0.097	0.188
4	0.095	0.184

The Croatian cement industry, together with other industries, will be participating in the implementation of the Kyoto protocol; therefore, it is important to work on the reduction of CO_2 emission.

2. Experimental procedures and results

Experimental studies are conducted in two stages:

1. Industrial studies on clinker production with the purpose of obtaining information about change in thermal and electric energy consumption, together with CO_2 emission dependant on the change of raw material structure;
2. Laboratory cement studies with the purpose of a higher percentage of replacement of clinker with slag and fly ash and an increase in cement strength of 46–48 MPa.

2.1. Clinker production

Industrial clinker is produced in rotary furnace with four target chemical structures (with lime saturation factor $[LSF]=100\ CaO/(2.8 \cdot SiO_2 + 1.2 \cdot Al_2O_3 + 0.65 \cdot Fe_2O_3)$ [12] (presented in Table 1). Aberrations of LSF are aimed at 92–99%, because with industrial clinker production in only one rotary kiln, it is complicated to produce clinker with a much bigger range due to mass production and large raw material and clinker depots.

CO_2 emission from raw material decarbonization is being developed according to the following chemical reaction:

$$CaCO_3(100\ g/mol) = CaO\,(56\ g/mol) + CO_2\ (44\ g/mol), \tag{1}$$

in which with stoichiometric calculation, we get the amount of CO_2 released from the raw material, with the factor 0.785 t CO_2/t CaO in clinker [7,10].

From industrially produced clinker, cements are prepared in the laboratory with 6% gypsum and strengths are determined after 28 days according to EN 196-1 (*Methods of Testing Cement—Part 1: Determination of Strength*).

Experimental studies are conducted in rotary kiln, where natural gas is the main energy source, and the quantity of CO_2 emission from natural gas combustion is explained through Eqs. 2–7 and is presented in Table 2. From 1 m^3 of natural gas (in vol.%: $CH_4=94.8$; $C_2H_6=1.81$; $C_3H_8=0.63$; $C_4H_{10}=0.34$; $C_5H_{12}=0.11$; $N_2=1.92$;

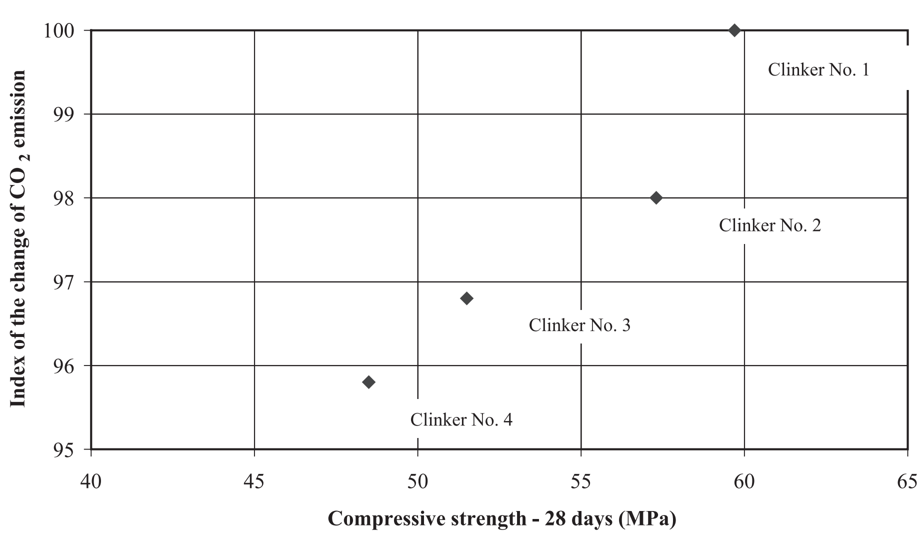

Fig. 1. The change of CO_2 emission in relation to 28-day compressive strengths for examined clinkers.

Table 3
Chemical structure of components

Component	LI (mass%)	CaO (mass%)	SiO_2 (mass%)	Al_2O_3 (mass%)	Fe_2O_3 (mass%)	MgO (mass%)
Slag	0.0	37.1	36.9	12.2	0.6	9.2
Fly ash	0.9	8.1	52.5	19.2	9.8	2.4

CO_2 = 0.33), 1.94 kg of CO_2 is released as the result of gas combustion [12]:

$$CH_4 + 2O_2 = CO_2 + 2H_2O \quad (2)$$

$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O \quad (3)$$

$$2C_3H_8 + 10O_2 = 6CO_2 + 8H_2O \quad (4)$$

$$C_4H_{10} + 6\,{}^1/_2O_2 = 4CO_2 + 5H_2O \quad (5)$$

$$C_5H_{12} + 8O_2 = 5CO_2 + 6H_2O \quad (6)$$

and, with the following equation, the total obtained CO_2 volume share is recalculated into mass:

$$m\ (CO_2) = V(CO_2) \cdot M(CO_2)/V^0 \quad (7)$$

The average annual figure from year 2002, effectuated in Našicecement, is used for specific electric energy consumption, and this figure is 72 kWh/t of clinker. For Croatia, 1 MWh is the equivalent of thermal energy consumption, which is 217 kg of transmitted CO_2 quantity. The implication is that during the production of 1 kg of clinker, 0.015 kg of CO_2 is released, which is caused by electric energy consumption. The share of CO_2 emission in observed clinkers can be calculated using the quantity of transmitted CO_2. The emission of CO_2 caused by raw material decarbonization is around 71%; by natural gas combustion, around 27%; and from electric energy consumption, around 2%. The results show that the biggest part of CO_2 emission is caused by raw material decarbonization, followed by natural gas combustion. Both are results of the change of target clinker structure, which requires different amounts of thermal energy for production. It was shown that the production of clinker is realising 98% of total realise of CO_2 in cement production. Therefore it is currently directing the course of further activities toward replacement of clinker in cement as much as possible.

The change in the quantity of total transmitted CO_2, compared with the change of compression strengths of clinker after 28 days, is presented in Fig. 1.

2.2. Cement production

During studies on cement production, the clinker with the greatest thermal energy consumption and CO_2 emission (clinker 1), to which slag and fly ash are added, is taken into consideration. They are added in a quantity that will give the approximate 28-day compressive strength to cement with clinker 4, with which the lowest thermal energy consumption and the lowest CO_2 emission are realized. Grinding of slag effects electric energy consumption, and ground slag and unground fly ash were chosen. The chemical structure of used components is presented in Table 3.

Reference cement 1 was ground with Blaine specific surface of 3449 cm^2/g. The distribution of particles of used components, as seen on laser granulometer (Malvern Instruments EASY Particle Sizer M3. 1), is presented in Fig. 2.

To determine the required electric energy for grinding, slag is separately ground under the same conditions as reference cement, and 20% of slag was ground together with the clinker. During grinding slag in laboratory conditions, greater electric energy consumption appears compared to reference cement grinding for similar fineness of ground material, and that is confirmed by joint grinding. Therefore, specific 40 kWh/t electric energy consumption for cement from industrial conditions of production is taken and specific electric energy consumption of slag is increased to 20%.

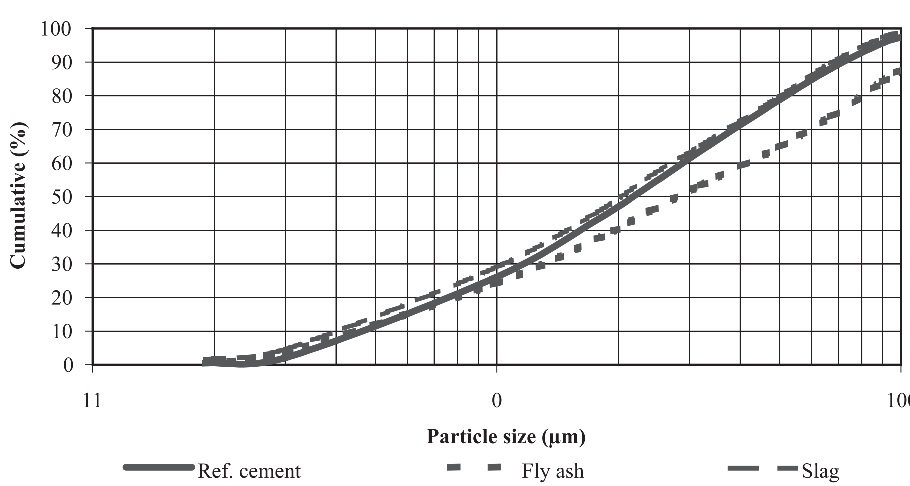

Fig. 2. Particles distribution of referent cement, slag, and fly ash.

Table 4
Mechanical characteristics and electric energy consumption of tested cements

Cement structure	Specific surface (Blaine, cm^2/g)	Water for standard consistency (Vicat, %)	Strength—2 days (MPa)		Strength—28 days (MPa)	
			Flexural	Compressive	Flexural	Compressive
Reference cement 1	3449	26.0	5.60	24.73	8.58	59.7
70% Reference cement + 30% slag	3356	25.8	4.12	15.43	7.98	47.2
75% Reference cement + 25% fly ash	3311	27.8	4.23	16.87	8.05	46.3
Cement 4	3420	26.0	4.27	17.24	8.03	48.5

Several cement mixtures are prepared, from which cements that have the same 28-day compressive strengths as clinker 4 are chosen for comparison. Cement studies are done according to EN196-1 (*Methods of Testing Cement—Part 1: Determination of Strength*), 196-3 (*Methods of Testing Cement—Part 3: Determination of Setting Time and Soundness*), and 196-6 (*Methods of Testing Cement—Part 6: Determination of Fineness*). Physical and mechanical characteristics of tested cements, together with specific electric energy consumption for grinding, are presented in Table 4.

Attained 28-day compressive strength of prepared cements can be seen in Table 4. Cement made of clinker 1, with the addition of 25% fly ash and 30% slag, has obtained strengths similar to cement made of clinker 4. Total transmitted CO_2 quantity for tested types of cements compared with the portion of clinker, together with the final compressive strengths, is presented in Fig. 3.

By adding 30% slag to the reference cement, CO_2 emission is decreased by 29%, and by adding 25% of fly ash, CO_2 emission is decreased by 24.6% compared with reference cement 1. CO_2 emission as equivalent of electric energy consumption is of a small quantity. That in the end has revealed the decrease of total CO_2 emission for almost the same percentage of replaced clinker either with addition that needed to be ground or ash in original state. Taking into consideration the average ratio of raw material/clinker conversion, i.e., 1.54, this implies that replacing 1 t of clinker (lesser production) in cement requires 1.54 t of raw materials.

3. Conclusion

1. The reduction of CO_2 emission in cement production is more achievable by using secondary raw materials that need to be ground or subsequently added to cement than by clinker production, and this results to the change of phase structure for the target cement quality, which is presented as 28-day compressive strength that comes to 46–48 MPa. In clinker production, the reduction of CO_2 emission is 4.3% (presented in Fig. 1), whereas by replacing of 25% and 30% clinker with mineral additions, CO_2 emission is reduced by 24.6% and 29%.
2. At the same time, decreasing the clinker in reference cement 1 resulted in decreased percentage of raw materials and same percentage of gas, whereas in the production of referential cement 4, there was a significant decrease in natural gas (7%) (Table 2).
3. In the future, the possibility of maximal replacement of clinker with mineral additions, using different minerals additions and combinations, which will give certain improvements in cement with regard to other characteristics (initial strengths, water need, etc.), should be the aim of further research.

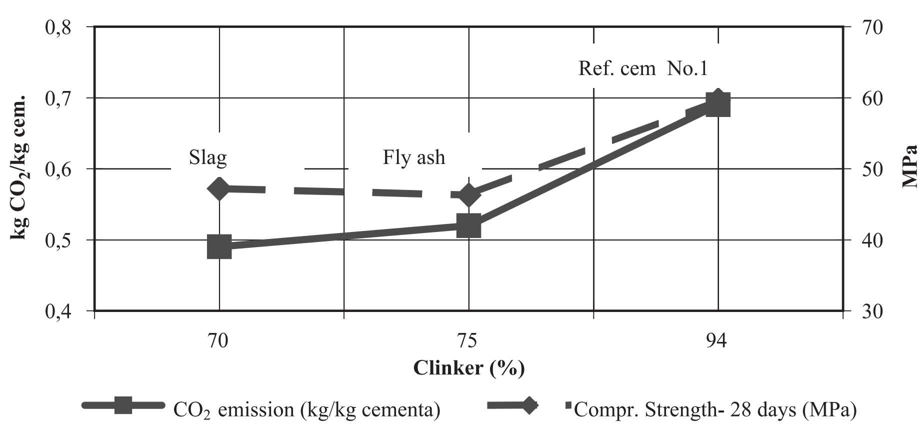

Fig. 3. Presentation of the change of CO_2 emission and 28-day compressive strengths in relation to the portion of clinker.

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