

Ecological and technological effects of using concretes with low Portland clinker

Mikołaj Ostrowski^{1,*}, *Paweł Pichniarczyk*², and *Grzegorz Kądziałowski*³

¹Sieć Badawcza Łukasiewicz – ICIMB Kraków

²Sieć Badawcza Łukasiewicz – ICIMB Warszawa

³Akademia WSB – Dąbrowa Górnicza

Abstract. Concrete with a low Portland clinker content involves the use of mineral additives as a cement component or as an additive in a concrete mix. The main factors influencing the increasing use of mineral additives in concrete technology are the advantageous development of the functional properties of the concrete mix, hardened concrete and a large impact on the ecological effects, including reduction of CO₂ emissions. The use of concrete with a low Portland clinker content is part of the strategy for sustainable development of the economy. This paper describes the technological and ecological effects of using silica fly ash and granulated blast furnace slag additives in concretes with a low Portland clinker content. The cement and concrete additives used were mechanically activated, which allowed to reduce the content of Portland clinker in concrete. A new generation superplasticizer was used in the research, enabling a low water-cement ratio to be obtained. The mechanical properties and ecological effects of the production and use of concretes with a low content of Portland clinker were determined, including the reduction of CO₂ emissions. Test results confirmed the very good mechanical properties of concrete with a high content of mechanically activated mineral additives. The research also showed an average of 3 times lower CO₂ emissions compared to reference concretes made of CEM I Portland cement without additives.

1 Introduction

Granulated blast furnace slag and silica fly ash have long been widely used as active ingredients that can significantly modify the properties of both concrete mix and hardened concrete [1-4]. With the development of technological processes in the production of cement and concrete, the use of these additives is more effectively and allows the production of high strength and durability concrete [5-7].

* Corresponding author: m.ostrowski@icimb.pl

The impact of mineral additives on the properties of the concrete mix and hardened concrete is determined by the hydraulic properties of granulated slag and/or the pozzolanic properties of silica fly ashes, which can be introduced as a Type II additives to concrete or with multi-component cements. Most publications about the activity of granulated slag and fly ash in the processes of hardening cement binders, associate these hydraulic and/or pozzolanic properties with their chemical composition and glass phase content [3, 4, 8, 11].

If the chemical composition of these additives is correct, the glassy phase content is a determining factor for the activity of granulated blast furnace slag and siliceous fly ash. Polish resources of fly ashes and slags are characterized by chemical composition and glassy phase content that guarantee their good activity. The degree of glass transition of granulated blast furnace slag exceeds 90%, and the content of the glassy phase in silica fly ash is 60 ÷ 80% [9-10].

The connections between the potential activity of blast furnace slag, fly ash and their chemical composition and glassy phase content are also determined by the degree of slag and fly ash fineness. The increase fineness of granulated slag leads to an improvement of activity. Modern milling cement technologies are more effective than oldest grinding methods and it is not a problem to effectively grind a slag cement to high specific surfaces. In the case of multi-component ash cements better properties of cement are related with high fineness of fly ash, what we can get by the dynamic separation method [4, 11-14].

With a very high degree of slag fineness and fly ash fineness, these materials can be very active additives and also perform a function similar to the role of reactive powders in modern concrete composite technologies [15, 16]. The use of ultra-fine grains of ground granulated blast furnace slag and silica fly ash as active additives for concrete allows shape a cement matrix with high strength properties [16, 17]. This effect can be caused by mechanical activation of the analyzed additives by increasing the fineness of granulated blast furnace slag by effective grinding method and dynamic separation of fine fractions of fly ash with particle size $D_{50} < 10\mu\text{m}$. Taking into account the activation methods described in this paper, the authors assumed objective to design and production concrete with compressive strength up to 100 MPa while the maximum reduction of the Portland clinker content- below 100 kg/m³. In the next phase of research, authors assume that positive results of mechanical properties must be related with tests of concrete performance. They should meet the requirements of durability properties of ordinary and special concretes, designed and manufactured for specific exposure classes, as defined in PN-EN 206 [18].

2 Materials and Methods

Concretes with a reduced Portland clinker content were made of CEM III / B 42.5L-LH / SR-NA, industrially produced by the method of joint mixing of components. The content of ground to high specific surface granulated blast furnace slag in cement was 70%. The specific surface area of cement was 5000 cm²/g (Tab. 1). The obtained test results were referred to control concrete made of CEM I 42.5 R (Tab. 1).

Table 1. Chemical composition of cements used in research [19].

Material	Ingredients content [% of mass]									
	LOI	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	Na ₂ O _{eq} *
CEM I 42,5R	2.92	19.65	5.14	2.46	63.89	1.27	2.94	0.11	0.77	0.62
CEM III/B 42,5 L-LH/SR-NA	0.78	33.07	6.68	1.62	51.52	2.80	2.41	0.41	0.58	0.79

*Na₂O_{eq} = % Na₂O + 0,658 · % K₂O

As a type II additive in concrete, silica fly ash category N and category S were used.

Category S fly ash was obtained as a result of mechanical activation consisting in the dynamic separation of a fine fraction from category N fly ash (Tab. 2). Changes in fly ash grain after the activation process are given in Figure 1. The improvement of fly ash fineness from 37.4% (for category N) to 2.8% (for category S) ensures a significant reduction in the D_{50} value from 40.9 μm to 7.7 μm . The effect of mechanical activation of ash, due to grain morphology and fineness, is very well illustrated by SEM photographs of fly ash N and S in Figure 2. Most of the fly ash S grains are spherical forms of small dimensions.

Table 2. Chemical composition of silica fly ash used in research.

Material	Ingredients content [% of mass]									
	LOI	NR	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O
Siliceous fly ash	2.63	79.8	51.37	27.80	6.55	2.97	2.51	0.23	0.68	3.54

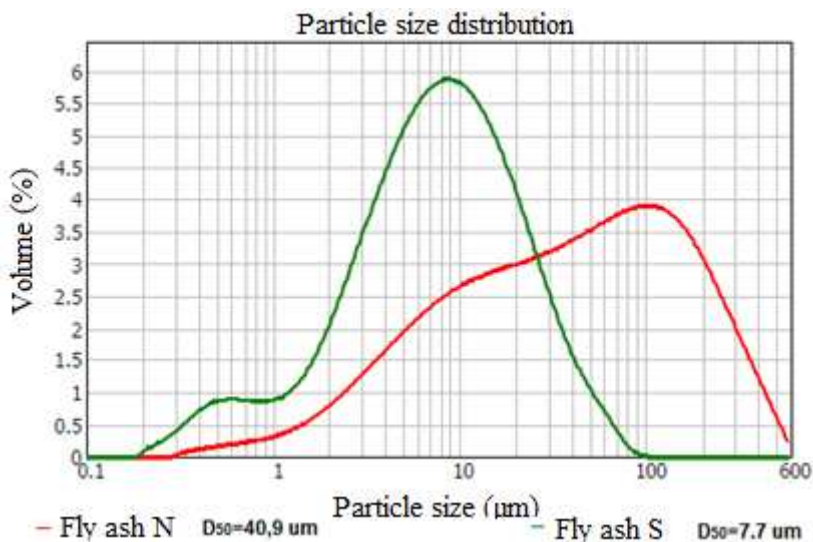


Fig. 1. Particle size distribution of silica fly ash category N and category S.

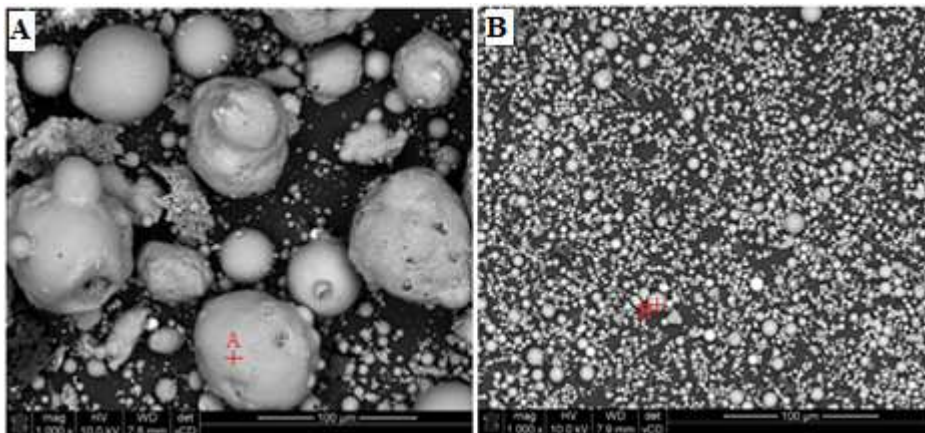


Fig. 2. SEM micrographs of silica fly ash. 1000x magnification. (A)- fly ash cat. N, (B)- fly ash cat. S

In order to shape the rheological properties of concrete mixes with a low content of Portland clinker and a large proportion of active pozzolanic-hydraulic additives, a new generation liquefaction admixture based on polycarboxylic ether was used. This type of admixture allows the production of concrete mixes with low water content and good fluidity. Therefore, a reduced w/c ratio causes more effective cement hydration and increasing the density of concrete which leads to improvement of concrete strength.

Concrete mixes with low Portland clinker were designed; 70 kg, 100 kg, 120 kg of clinker in 1 m³ of concrete mix. These concrete mixtures were made of CEM III/B 42,4L-LH/SR-NA cement and with the addition of N and S silica fly ash, as type II additive, with the aim of getting good rheological and long-term mechanical properties. Concrete was made at various w/c ratio with the addition of the new generation GleniumSky 430 superplasticizer. Portland cement CEM I 42.5 R was used in the control concrete, without mineral additives. Three reference concrete were designed, assuming 450, 360 and 280 kg/m³ of cement in concrete mix, respectively for high strength concretes, reference concrete according to standards and concrete containing a minimum amount of cement, due to the exposure classes according to PN-EN 206-1 [18].

Concrete mixes were prepared from natural basalt, gravel and sand aggregates.

Concretes containing clinker in an amount of 120, 100 and 70 kg/m³ met the requirements for cement content and w/c ratio, according to requirements for exposure classes in standard PN-EN 206-1 [18].

The compositions of concrete mixes are presented in Table 3. The properties of designed concretes with a reduced content of Portland clinker was carried out in terms of compressive strength [18].

Table 3. Composition of concrete mixtures.

Concrete Component	B120N	B120S	B120 CEM I	B100N	B100S	B100 CEM I	B70N	B70 CEM I
CEM III/B 42,5L [kg/m ³]	400	400	-----	332	332	-----	233	-----
Silica fly ash* [kg/m ³]	N-125	S-125	-----	N-70	S-70	-----	N-118	-----
Cement _{eq} = C + 0,4 p [N3]	450	450	-----	360	360	-----	280	-----
CEM I 42,5R [kg/m ³]	-----	-----	450	-----	-----	360	-----	280
Water [kg/m ³]	167	167	167	162	162	162	154	154
Sand 0-2 mm [kg/m ³]	655	655	690	705	705	730	620	650
Basalt 2-8 mm [kg/m ³]	550	550	580	590	590	610	-----	-----
Basalt 8-16 mm [kg/m ³]	635	635	670	680	680	705	-----	-----
Gravel 2-8 mm [kg/m ³]	-----	-----	-----	-----	-----	-----	375	395
Gravel 8-16 mm [kg/m ³]	-----	-----	-----	-----	-----	-----	415	435
Gravel 16-32 mm [kg/m ³]	-----	-----	-----	-----	-----	-----	470	495
w/s(w/c+0,4p)	0,37	0,37	0,37	0,45	0,45	0,45	0,55	0,55
Portland clinker [kg/m ³]	120	120	430	100	100	340	70	270
B120/100/70/N/S - concrete mixtures containing 120,100,70 kg/m ³ of clinker made of CEM III/B 42,5L cement, containing 70% slag and silica fly ash category N or S B120/100/70/CEM I - reference concretes containing 450,360,280 kg/m ³ CEM I 42,5R cement without additives * N – silica fly ash category N and S – silica fly ash category S according to PN-EN 450-1:2012								

The scope of testing concrete mixes included determination of: density, flow (consistency) and loss of consistency over time, air content. The consistency of concrete mixtures was tested using the cone fall method according to PN-EN 12350-2: 2011 [20]. The air content was tested using the pressure method according to PN-EN 12350-7: 2011 [21]. Compressive strengths of concretes after 2, 7, 28, 90 and 360 days were tested on 15cm cubic samples, according to PN-EN 12390-3:20011 [22].

3 Results

The results contained in Table 4 shows that to ensure the assumed consistency and reduced water-cement ratio, the required amount of a superplasticizer is clearly smaller for concrete mixtures with a low Portland clinker, compared to the reference mixtures of CEM I 42.5R. This relate should be linked with the use of high-quality silica fly ash, which shapes better the rheological properties of the concrete mix.

The air content in all concrete mixes was similar and amounted 1.8% to 2.0%, i.e. below the limit of 2% for a properly prepared concrete mix (Tab.4).

Concrete mixes containing a very low amount of Portland clinker 70-120 kg/m³ compared to reference mixtures of CEM I cement also show greater stability in maintaining a constant consistency over time, maintaining the assumed consistency class of the S4/S3 mix for up to 60 min (Tab.4).

Table 4. Properties of concrete mixes.

Properties	Description of concrete							
	120N	120S	120 CEM I	100N	100S	100 CEM I	70N	70 CEM I
Superplasticizer PCE [% m.c]	0.80	0.65	1.65	0.40	0.40	0.80	0.80	1.20
Initial consistency [mm]	160	150	150	170	170	180	165	130
Consistency after 30 min. [mm]	160	150	150	160	170	170	160	130
Consistency after 60 min. [mm]	140	140	130	160	160	150	150	100
Air content [%]	2.0	2.0	2.0	1.8	2.0	1.8	1.8	2.0
Density [kg/dm ³]	2.49	2.49	2.49	2.49	2.48	2.48	2.39	2.38

The results of compressive strength of low Portland clinker concrete 70-120 kg/m³ of concrete mix are compiled in Table 5 and Figure 3. The strength of concrete 120N/S with a Portland clinker content of 120 kg/m³ after 2 days of hardening is clearly lower in comparison to the reference concrete made of CEM I 42.5R cement. After further hardening periods very large increases in concrete strength are observed. Already after 7 days the 120N/S with a Portland clinker content of 120 kg/m³ concrete compressive strength is 55 MPa and achieves the strength of reference concrete containing 450 kg of cement in 1 m³ of concrete mix. After 28 days the relative strength of 120N/S concrete is about 140% of the reference concrete strength (Fig. 4). Compressive strength of concrete 120N/S achieves 89/92 MPa after 28 days corresponds to the strength class of concrete C60/75 [18]. 120CEM I reference concrete meets the requirements for strength class C50/60. Large increases in strength for 120N/S concrete are also observed in later hardening periods. The strength of concrete 120S exceeds 100 MPa after 90 days (Tab.5, Fig.3).

The increase dynamics of strength 120N/S concrete with the 0.37 water-cement ratio were confirmed for the 100N/S concrete series containing 100 kg of Portland clinker. At a w/c = 0.45, 100N/S concretes show very low strength after 2 days of hardening and large increases after further periods. Standard strength after 28 days of 100N/S concrete reaches 70 MPa, clearly exceeding the strength of reference concrete containing 360 kg of Portland

cement CEM I 42.5R (Tab. 5, Fig. 3, Fig. 5). The concrete 100N/S meet the requirements for strength class C50/60 after 28 days (Tab.5).

The dynamics of hardening of 70N concrete containing 70 kg of Portland clinker and the addition of category N fly ash confirms the relations discussed for 120N/S and 100N/S concretes. At a w/c=0.55, the early strength of 70N concrete after 2 days is only 10 MPa, with a large increase in strength after further hardening periods (Tab. 5, Fig. 3). The relative strength of 70N concrete after 28 days of hardening is 127% of reference concrete strength 70CEM I containing 280 kg of CEM I 42.5R (Fig. 6). The absolute strength of 70N concrete after 28 days is 60 MPa and meets the requirements for the strength class of structural concrete C40/50 (Tab.5, Fig.3).

Table 5. Compressive strength of concretes.

Description of concrete	Compressive strength [MPa]					Concrete strength class [18]
	2 days	7 days	28 days	90 days	360 days	
120 N	20.6	55.1	92.0	96.2	112.3	C50/60
120 S	18.1	55.3	89.0	104.4	110.6	
120 CEM I	39.5	55.8	64.3	71.2	79.6	
100 N	12.4	35.3	68.9	82.4	87.9	C40/50
100 S	12.6	33.7	70.9	82.3	90.0	
100 CEM I	31.3	50.3	60.3	66.3	73.1	
70 N	10.4	30.2	59.6	72.1	81.7	C25/30
70 CEM I	20.8	34.9	46.8	59.0	71.0	

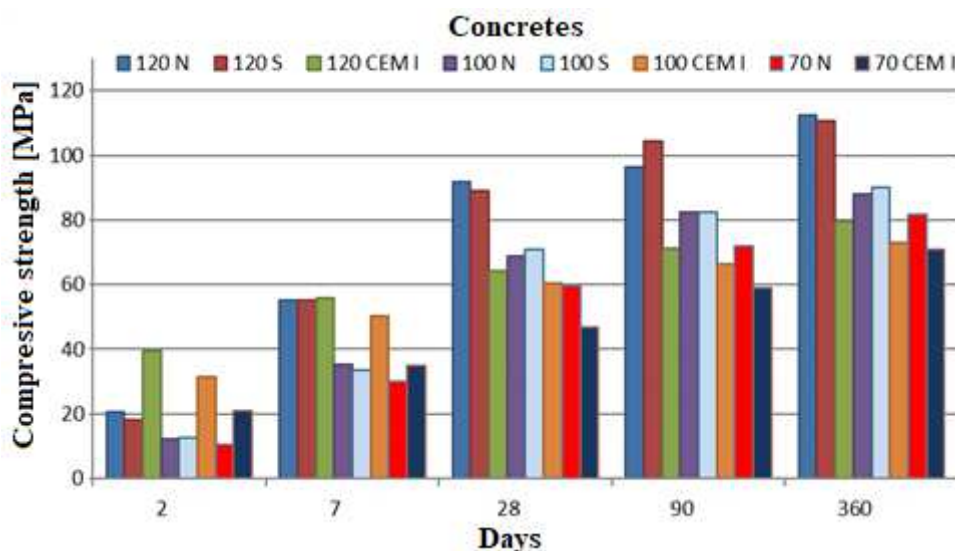


Fig. 3. Compressive strength of concretes

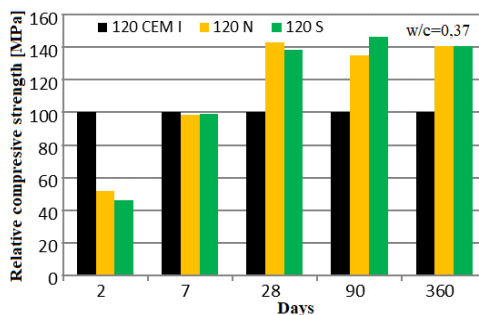


Fig. 4. Relative compressive strength of 120N/S concrete containing 120 kg of Portland clinker in 1 m³ of concrete.

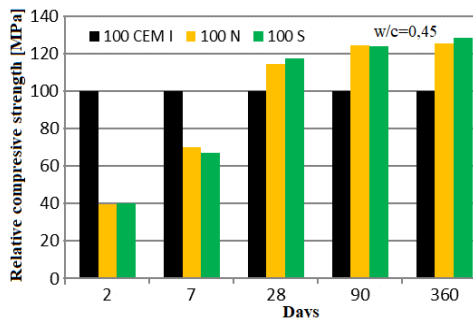


Fig. 5. Relative compressive strength of 100N/S concrete containing 120 kg of Portland clinker in 1 m³ of concrete.

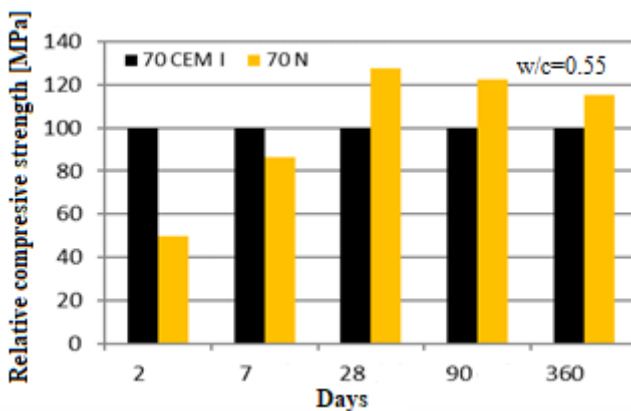


Fig. 6. Relative compressive strength of 70N concrete containing 70 kg Portland clinker in 1 m³ of concrete.

The use of fly ash and granulated slag as substitute of Portland clinker (cement) in concrete has an impact on reducing CO₂ emissions. The CO₂ reduction effect can be calculated per unit of product, i.e. cement at concrete and cement producers. Replacing 1% of clinker in cement with ash or slag can reduce CO₂ emissions by 9.1 kg/t of cement. Accordingly, the transition from the production of CEM III/A cement containing 50% slag to the production of CEM III/B cement containing 70% slag gives the effect of reducing CO₂ emissions to 182 kg/t of cement. This is the basic environmental effect of the increased use of slag and ash in multi-component cement technology. This effect can be more increased if cement used in a concrete has a low content of clinker and additionally the fly ash is used as a type II additive in concrete. The scale of effects resulting from the increased content of non-clinker components in concrete is presented in Fig. 7, where the amount of CO₂ reduction is shown for concrete with a large addition of mechanically activated fly ash and slag. Compared to reference concrete made of CEM I, CO₂ emissions are on average 3 times lower.

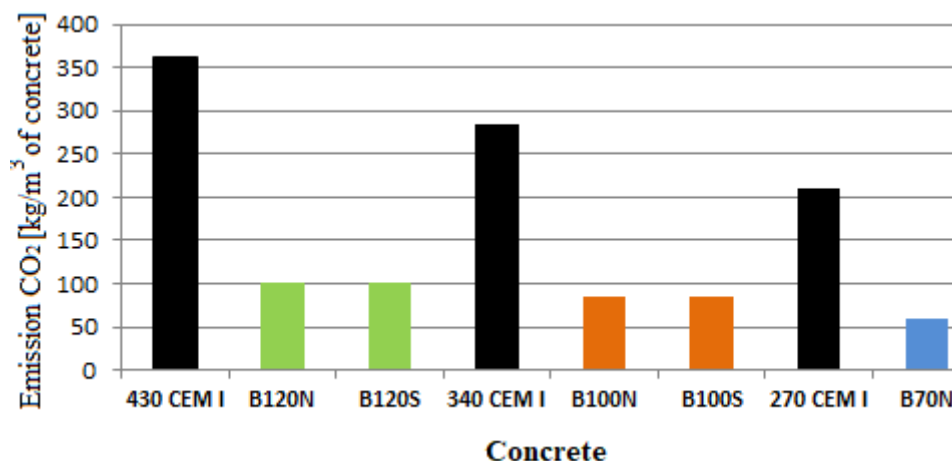


Fig. 7. Reduction of CO₂ from production of concrete with a low content of Portland clinker.

Data used in the calculation:

1. 850 kg CO₂/t of clinker – the amount of CO₂ emission in the dry production process of 1 ton of clinker from natural raw materials.
2. 93% - the amount of clinker content in CEM I as reference cement;
3. 70% - the amount of slag content in cement CEM III/B 42.5L.

4 Discussion

Granulated blast furnace slag and high-quality silica fly ash are valuable components of concrete with a low content of cement clinker.

An important component of concrete with a low content of cement clinker is suitable quality fly ash. Good quality fly ash reduces water content and improves consistency, ensuring good workability with a reduced water-cement ratio in the concrete mix.

In concretes with a low w/c ratio (below 0.4), fly ash of the S category is particularly useful. The use of this type of fly ash allows to significantly improve rheological properties (reduction of the water requirement of the binder in concrete) and strength in longer hardening periods (over 28 days).

By using CEM III/B metallurgical cement with a specific surface area of approx. 5000cm²/g, silica fly ash of categories N and S containing up to 5% roasting loss (category A) and the latest generation superplasticizers, we can obtain fully useful structural concrete in the strength class from C50/60 (clinker content 120 in m³ of concrete mix), through class C40/50 (clinker content 100 kg/m³) to class C 25/30 (clinker content 70kg/m³).

The hardening dynamics of concretes containing 120 kg/m³ of Portland clinker confirms the possibility of designing high-strength concretes using the effect of mechanical activation of pozzolanic-hydraulic additives introduced into the concrete mix.

The production and use of concrete with a low content of cement clinker in construction allows achieving significant ecological effects: CO₂ emission reduced by almost three times compared to concrete made of CEM I Portland cement, management of heavy secondary raw materials from the energy and metallurgy industries and reduction of the surface area for landfills.

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