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Green Concrete Based on Quaternary Binders with Significant Reduced of CO_2 Emissions

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Abstract: The article presents studies of plain concretes prepared based on a quaternary binder containing various percentages of selected supplementary cementitious materials (SCMs). The possibilities of nanotechnology in concrete technology were also used. An additional important environmental goal of the proposed solution was to create the possibility of reducing CO_2 emissions and the carbon footprint generated during the production of ordinary Portland cement (OPC). As the main substitute for the OPC, siliceous fly ash (FA) was used. Moreover, silica fume (SF) and nanosilica (nS) were also used. During examinations, the main mechanical properties of composites, i.e., compressive strength (f_{cm}) and splitting tensile strength (f_{ctm}), were assessed. The microstructure of these materials was also analyzed using a scanning electron microscope (SEM). In addition to the experimental research, simulations of the possible reduction of CO_2 emissions to the atmosphere, as a result of the proposed solutions, were also carried out. It was found that the quaternary concrete is characterized by a well-developed structure and has high values of mechanical parameters. Furthermore, the use of green concrete based on quaternary binders enables a significant reduction in CO_2 emissions. Therefore quaternary green concrete containing SCMs could be a useful alternative to plain concretes covering both the technical and environmental aspects. The present study indicates that quaternary binders can perform better than OPC as far as mechanical properties and microstructures are concerned. Therefore they can be used during the production of durable concretes used to perform structures in traditional and industrial construction.

Keywords: green concrete; quaternary binder; siliceous fly ash (FA); silica fume (SF); nanosilica (nS); SCMs; mechanical properties; microstructure; C-S-H phase; reduction of CO_2 emission

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1. Introduction

For many years, the cement and concrete industry has faced a number of challenges, which include, among other things, the depletion of fossil fuel reserves, constant shortage of raw materials for production of composites, or abnormal growth in demand for this type of construction material, i.e., the concrete. Among the many problems associated with the production of concrete using traditional methods, concerns are also focused in terms of its negative impact on the natural environment. Counteracting climate change is currently one of the most important elements of world politics, e.g., [1].

Therefore, practically all environmental aspects of concrete structures are considered in the following three categories, e.g., [2–18]:

- consumption of natural resources;
- consumption of energy;
- CO_2 emission.

Unfortunately, the production of ordinary concrete in its traditional form has a negative reflection practically in all of the fields listed above. Manufacturing of concrete consumes a huge quantity of natural resources, mainly for the preparation of raw materials to burnout of Portland clinker, but also as an aggregate for concrete [19–21]. In addition, the production of ordinary Portland cement (OPC) involves considerable energy consumption, both thermal and electrical [22–24], and evident air pollution by greenhouse gas (GHG) emission [25–28].

Nowadays, the most attention is paid to the greenhouse effect, to which the emission of CO_2 largely contributes. It covers approximately 55% of all GHG emissions. Because human activity increases the concentration of GHG in the atmosphere (mainly CO_2) that hinder the emission of heat into outer space, thereby causing dangerous climate change, so in the field of pro-ecological activities, there are, among other things, intense efforts to reduce as much as possible emission of this harmful oxide [29–31].

It should be noted that currently, in almost all industry sectors, efforts are observed to quantify GHG emission, which allows identification of factors and production stages that pollute the environment the most. Such activities are undoubtedly the first step towards the implementation of solutions reducing their emission. Regarding the production of concrete it should be added that the CO_2 emission in this process concerns mainly burning the Portland clinker, which is necessary for the production of OPC, e.g., [32–34]. This problem will be further discussed in Section 2.

One of the options for reducing emissions of CO_2 produced in the processes of preparation of the main binder, i.e., OPC, there is limiting the share of clinker cement in its composition in favor of other useful materials. According to the assumptions, production of low-emission cement would be possible by lowering the clinker/cement ratio to a level of 0.7, which is expected in 2050. Currently, although this rate is gradually declining, it is still clearly disadvantageous. In the year 2000, the rate was 1.06, while currently has a value of 0.9 (Table 1). This value, although not as high as several decades ago, still does not correspond to the trends based on green technologies in the cement industry [35–40]. This is confirmed by the latest data on the production of OPC and Portland clinker in states with the largest global share, and the global average in this industry, which are summarized in Table 1 [41].

Table 1. World production of cement and clinker in 2019 [41].

Country	Production of Cement (mln ton)	Share(%)	Production of Clinker (mln ton)	Share(%)	Clinker/Cement Ratio
China	2200	53.7	1970	53.2	0.90
India	320	7.8	280	7.6	0.88
Vietnam	95	2.3	90	2.4	0.95
United States	89	2.2	103	2.8	1.16
Egypt	76	1.9	48	1.3	0.63
Indonesia	74	1.8	78	2.1	1.05
Iran	60	1.5	81	2.2	1.35
Russia	57	1.4	80	2.2	1.40
Republic of Korea	55	1.3	50	1.4	0.91
Brazil	55	1.3	60	1.6	1.09
Japan	54	1.3	53	1.4	0.98
Turkey	51	1.2	92	2.5	1.80
Poland	19	0.5	13	0.4	0.68
Other Countries	881	21.5	707	19.1	0.80
World total	4100	100	3700	100	0.90

A solution that has been meeting the above problems for some time, is using so-called green concrete to make concrete structures [42–48]. Structures made in this manner are environmentally sustainable concrete structures, which are characterized by their overall impact on the ecosystem of humans and animals being as limited as possible. It should be added that in case of such construction, a holistic approach to their design and implementation is used. The impact of buildings constructed in this way is assessed at all stages of operation, involving five phases. They are summarized and described in details in Table 2.

Table 2. Implementation phases in a complete cycle of a typical concrete structure [49,50].

Phase Number	Stage	Activities
Phase 1	Place of raw material acquisition	• Extraction of raw materials, • production of components, • transport to concrete plant.
Phase 2	Concrete plant	• dosing of ingredients, • production of mix, • transport to construction site.
Phase 3	Construction	• laying the mix, • consolidation, • care of elements.
Phase 4	Period of facility use	• operation, • maintenance, • repairs and overhauls.
Phase 5	"The second life of the structure"	• demolition, • reuse, • recycling.

It should therefore be noted that green concrete is not defined universally, however, when used to build the structure, it must meet the requirements for strength and durability, whereas its ingredients must be environmentally friendly materials (Table 2).

Therefore, in modern technology of green concrete, a great interest of scientists and practical engineers concerns the possibility of modifying the microstructure of cement-based materials by using chemically active mineral additives. These include natural pozzolans, siliceous and calcareous fly ash, silica fume, granulated blast furnace slag, lime powder, and other materials that replace the cement binder in the composition of the concrete mix, e.g., [51–69]. There is also the increasingly used potential of nanotechnology, in which green concrete nanoadditives are used included in its composition, such as e.g., nanosilica, carbon nanotubes, and active chemical nanoadditives, e.g., [70–73]. Both traditional concrete additives and nanoadditives that are part of modern cement matrix composites are referred to as supplementary cementitious materials (SCMs) [74–81].

The use of SCMs in the production of concrete composites promotes sustainability in the concrete industry [82]. However, due to the fact that in the vast majority of countries in the world, energy generated for industrial and domestic needs is still produced by burning hard coal, siliceous fly ash (FA), which is a by-product of these processes, is the main additive to ordinary and green concrete composites currently produced, e.g., [83–85]. This is evidenced, among other things, by the amount of these by-products generated annually at almost one billion tons [86,87]. Therefore, a serious issue becomes the FA management in such a way that they do not adversely affect the environment because, in some respects, they are hazardous materials, e.g., [88,89]. In addition, such measures result in a reduction of the basic binder used in the production of the concrete composites, i.e., the OPC, in the composition of the concrete mix. Consequently, this results in: lower costs of producing such materials [90], reduced consumption of thermal and electric energy [91] and, what is important, a marked reduction in emission of harmful GHG [92]. Considering the above aspects, it must be stated that the utilization of FA also carries an evident pro-ecological factor, e.g., [93–95].

Utilization of finely grained FA in green concrete technology brings considerable advantages, as demonstrated in many previous publications, e.g., [96,97]. Substitution of OPC by this material in an amount up to 20% contributes to the improvement of parameters of mature concrete composites, such as compressive and tensile strength [98,99], fracture toughness [100–102], heat resistance [103], abrasion and erosion resistance [104], resistance to vibration and impact loads [105–108], and rheological properties of the material [109,110]. Substitution of OPC using FA also causes a reduction in the negative effects in structures made on the basis of such a binder due to the corrosive effects and expansion [111–113], electrical resistivity [114] and the dynamic loads [115–118].

However, the concept of green concrete is undergoing intensive development and is presenting more and more opportunities for the use of these sustainable materials in the concrete industry. One of the most effective solutions is the possibility of supplementation cement binder with several active modifiers at the same time. Such a solution allows both the use of more binder substitutes, and the possible use of a synergistic interaction of individual pozzolanic active mineral additives with each other. You can find works in the literature presenting promising test results of green concrete carried on cement binders with different content of additives, starting from the simplest—binary [119–122] by ternary [123–125], and ending with the most technologically advanced—quaternary [126–134], or even quinary [135].

Therefore, this article proposes a solution involving modification of the concrete material with the main mineral additive, i.e., FA and the two types of silica-based additives. Supplementing the composition of the binder in the composites were, therefore, traditional non-compacted silica fume (SF), and the resulting from the modern concept of what is nanotechnology—nanosilica (nS). A proposal for green concrete made on the basis of quaternary binders formulated into various proportions of the above mineral additions is one of the possibilities for effective reduction of CO_2 and a significant reduction in the carbon footprint created in the production of ordinary concrete [135,136].

2. CO_2 Emission in the OPC Production Process and Possibility of Its Reduction by Using Green Concrete Based on Quaternary Binders

The World cement production generates around 7% of total CO_2 emissions globally, e.g., [137]. This harmful gas is produced during the three following operations (Figure 1):

- 50% is generated by the decomposition of limestone,
- 40% is because of fossil fuel combustion,
- 10% is contributed due to raw material transportation as well as electricity generation.

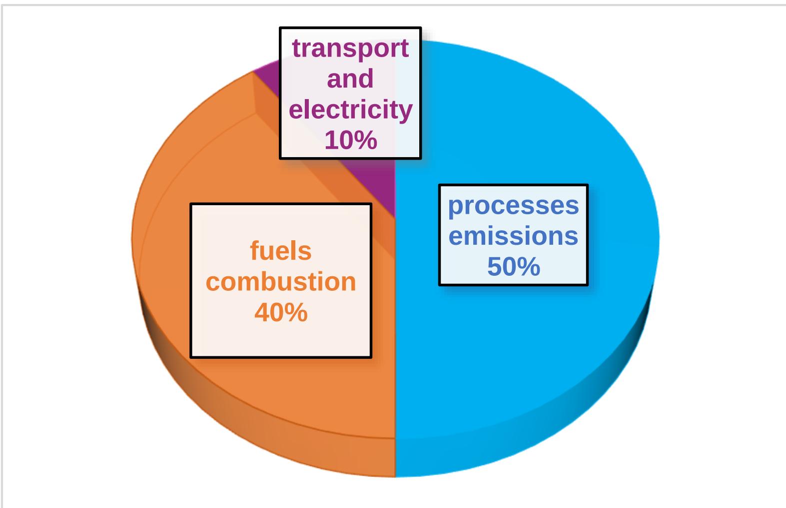


Figure 1. Operations in which CO_2 is generated in the OPC production process [49].

Generally, carbon dioxide in cement production processes is emitted from two basic direct sources, i.e., the process of decarbonization of calcium carbonate and fuel combustion, and two indirect sources, i.e., the production of electricity used in cement plants and transport.

The burning of Portland clinker and the subsequent production of OPC involves many complex technological operations. According to [49], Figure 2 provides a detailed diagram of these processes indicating the stages in which CO_2 emissions occurs.

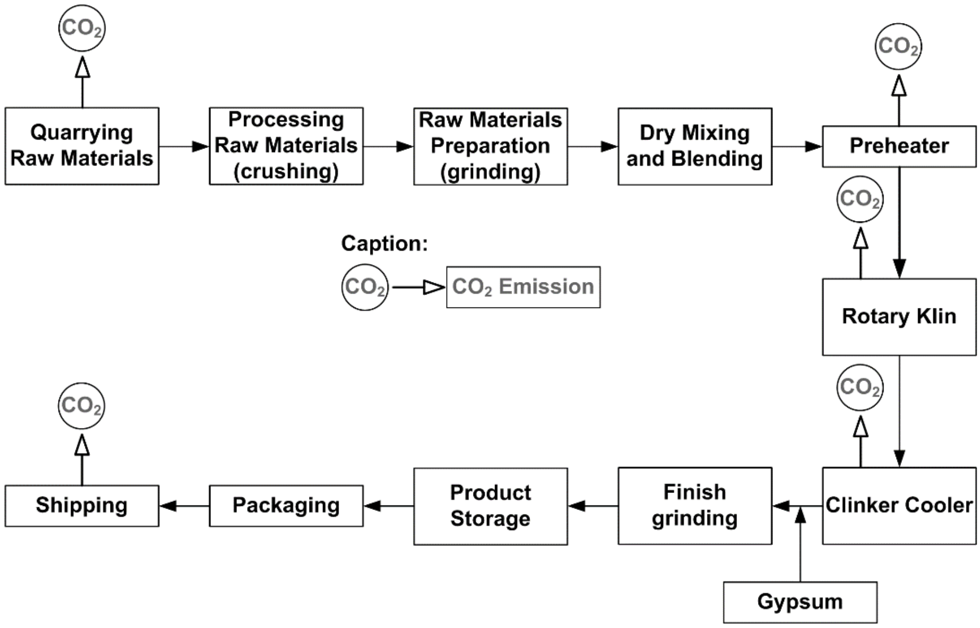


Figure 2. Detailed diagram showing the steps of OPC manufacturing and stages during which CO_2 is emitted [49].

The complex and multi-stage OPC production process causes that the production of one tonne of cement emits according to various sources from 0.8 to 1.0 tonne of CO_2 [138,139]. However, a simple relationship can be found between these processes when taking into account the so-called carbon footprint of concrete and all stages of cement production [140], i.e., 1 tonne of OPC $\equiv$ 1 tonne of CO_2 [141]. Based on this relationship and the data contained in Table 1, it can be concluded that currently, in global terms, approx. 4.1 billion tonnes of CO_2 is produced during the production of cement.

Therefore, the reduction of CO_2 emissions, generated during the burning of Portland clinker has been an important environmental problem for a long time. In this regard, more and more new research and theoretical simulations as well as novel implementation activities to reduce this negative effect are carried out, e.g., [142–145]. Their primary goal is to reduce as much CO_2 emission as possible, which is generated in OPC production at almost all stages (Figure 2). Therefore, there is an increasing development of modern binders based on the concepts of sustainable construction, e.g., [12–14,33,146–149].

One of such solutions is the possibility of partial replacement of the OPC with one or more together active mineral additives. Part of the materials used in this way, such as FA are troublesome industrial wastes. Hence, the benefits of such actions are multiplied, even turning into multiplicative relations.

As demonstrated in the following papers [150–158] the benefits associated with the implementation of substitutes for cement binder in the composition of the concrete mix are also related to their positive influence on the processes correlated with the formation of a compact structure in the concrete composites. Therefore, the following article presents a proposal for the use as a components of the green concrete of two pozzolanic active mineral additives, i.e., FA and SF in combination with nanoadditives, i.e., nS. Then, efforts were made to assess the benefits of such material modification, both for improved performance of composites analyzed and the possibility of reducing CO_2 emission.

Concretes made with applying the quaternary binder were tested for:

- their basic mechanical parameters analysis;

- changes that have occurred in their structure as a result of the substitution of cement binder by different compositions of supplements applied;
- reduction of harmful emissions of CO_2 by reducing the amount of OPC in the total weight of the binder used.

3. Experimental Section

3.1. Materials

OPC 32.5 R as per EN 197-1:2011- Cement—Part 1 standard [159], class F FA, non-condensed SF, and Konasil K-200 nS in different proportion were used for the preparation of quaternary blends. It was also assumed that:

- the total amount of the binder in all composites will be constant;
- amount of the binder substitute at 10% and 5% will be constant for SF and nS, respectively;
- a variable parameter will be the addition of FA, which will replace the OPC in the amount of 0, 5, and 15%;
- the same water-binder ratio at level 0.4 in all mixtures.

Table 3 provides where all SCMs used came from.

Table 3. The origin of SCMs used.

Origin	Kind of SCMs			
	OPC	FA	SF	nS
Country		Poland		South Korea
City	Chełm	Puławy	Łaziska	Seul
Manufacturer	Cement Plant	Thermal-electric power station	Ironworks	OCI Chemical Company Ltd.

The chemical constituents of SCMs used are shown in Table 4, whereas the main physical properties of these materials were presented in Table 5. The XRF method supported by Epsilon 3× spectrometer (Malvern Panalytical, Malvern, UK) was used to evaluate the chemical composition of all binders, whereas laser granulometry using measuring device Masterizer 3000 and measuring range 0.01–3500 μm were used (Malvern Panalytical, Malvern, UK) to obtain average particle diameter of SCMs used.

Table 4. Chemical constituents of SCMs used.

Chemical	Component (wt %)			
	OPC	FA	SF	nS
SiO_2	15.00	55.27	91.90	>99.8
Al_2O_3	2.78	26.72	0.71	-
Fe_2O_3	2.72	6.66	2.54	-
CaO	71.06	2.35	0.31	-
K_2O	1.21	3.01	1.53	-
SO_3	4.56	0.47	0.45	-
MgO	1.38	0.81	1.14	-
P_2O_5	-	1.92	0.63	-
TiO_2	-	1.89	0.01	-
Ag_2O	-	0.10	0.07	-
MnO	-	-	0.26	-
Cl	0.08	-	0.28	-

Table 5. Physical characteristics of SCMs used.

Physical Parameter	Kind of SCMs			
	OPC	FA	SF	nS
Specific gravity (g/cm^3)	3.11	2.14	2.21	1.10
Blaine's fineness (m^2/g)	0.33	0.36	1.40	200
Average particle diameter (µm)	40	30	11	0.012
Color (visually)	Light gray	Dark gray	Black	White

The proposed selection of components for the implementation of concretes was aimed at assessing the synergy of the interaction of individual additives with each other in the direction of improving the mechanical parameters and microstructure of composites. The control concrete (REF) did not contain any binder substitutes, while in the Q series concretes, efforts were made to determine the effect of FA on the analyzed parameters of concretes containing SF and nS with a constant content of these modifiers. For this purpose, the concrete of the Q1 series was, in a sense, a quasi-reference concrete, i.e., with 0% FA content, in relation to materials with the OPC substitute by FA at 5% and 15% respectively in the series of concretes Q2 and Q3.

Moreover, coarse aggregate (natural gravel 2–8 mm size with specific gravity 2.65 and compressive strength 34 MPa), fine aggregate (pit sand, maximum size 2.00 mm with specific gravity 2.60 and compressive strength 33 MPa), plasticizer, Basf Liquol BV-18, and the laboratory pipeline water for preparation all mixtures were used. Table 6 provides information on various mix proportions of SCMs with OPC for reference (REF) series (100% OPC), and quaternary binders (Q series) considered for the present study.

Table 6. Various mix proportions of OPC and SCMs used for the experimental work.

		Proportion of Binder Components (%)			
Mix	Type of Binders	OPC	FA	SF	nS
REF	Reference	100	–	–	–
Q	Quaternary				
Q1		85	0	10	5
Q2		80	5	10	5
Q3		70	15	10	5

3.2. Methods

Compressive strength (f_{cm}) and splitting tensile strength (f_{ctm}) of the hardened concrete as per standard procedure given in EN 12390-3: 2011+AC: 2012 [160] and EN 12390-6: 2009 [161] were measured. Standard concrete cubes of dimensions 150 × 150 × 150 mm^3 were prepared and tested in 300 T capacity (Walter + Bai ag, type NS19/PA1; Löhningen, Switzerland). The rate of loading was kept between 0.5 to 0.8 MPa/s. In order to ensure the repeatability of test results, six specimens for all composites and both mechanical tests were prepared and reported after 28 days of curing.

In addition to macroscopic examinations, structural analysis of all the composites was also carried out. SEM study was conducted to identify the morphological characteristics of the concrete mix prepared from quaternary binders. In the course of the micro-structural experiments, the following assumptions were made:

- the test specimens had rectangular shapes and approximate dimensions of 10 × 10 × 3 mm^3;
- the test was conducted using a QUANTA FEG 250, which was equipped with an energy dispersive Spectroscopy (EDS EDAX);
- for each of the composites, the images were taken at the same magnifications, i.e., 8000 and 16,000 times and the same reference scales, i.e., 20, and 10 µm;
- for each type of material, the images were taken on six samples;

- 30 images were taken for each sample, from which representative images were selected;
- on the SEM images, the following were marked or described: areas with the FA grains, areas with clearly distinguishable phases, e.g., calcium silicate hydrate (C-S-H), calcium hydro oxide (CH), or ettringite (E).

In addition to assessing strength parameters and microstructure in concretes modified with pozzolanic additives, the additional goal of the study was to determine the environmental benefits related to possible limitation of CO_2 emissions as a result of reducing the use of OPC in the composition of the concrete mixture and replacing this basic binder with useful mineral additives. Assuming that the annual OPC production is 4.1 million tonnes (Table 1), and considering the fact that production of 1 ton of the binder leaves CO_2 generated to atmosphere approximately in the same amount—as discussed in Section 2—attempts were made to estimate the limit that can be achieved in the emission of this oxide by the replacement of OPC with proposed SCMs in various formulations rates.

The possible reduction of CO_2 emissions, in the case of using concretes with the proposed compositions, was therefore obtained on the basis of the percentage reduction in the use of the OPC in each of the composites. Since the amount of OPC produced is practically equal to the amount of generated CO_2—therefore, globally, the percentage reduction in OPC consumption will correspond to the same amount of reduction in CO_2 emissions.

4. Results and Discussion

4.1. Strength Parameters

Table 7 provides the main mechanical parameters with standard deviations (δ) of analyzed composites. In quaternary concrete Q2 and Q3, it was observed that both strengths of the concrete reduced with increased FA percentage level from 5 to 15%, which can be attributed to the properties of FA that suppress the heat of hydration of cement and, in turn, requires a longer curing period for pozzolanic reactions [47,149,150]. Nevertheless, concrete of Q2 series, i.e., with 5% FA additive, in combination with 10% of SF additive and 5% of nS additive had the best strength parameters. Equally good results of modification were observed in the Q1 concrete series, i.e., with the addition of SF and nS only. Definitely the lowest strength was recorded in the case of the reference concrete (Table 7). Therefore, it can be clearly stated that the OPC substitution by each proposed composition of active pozzolan mineral additives brings measurable benefits in the results of the basic mechanical properties of the quaternary green concrete.

Table 7. Compressive strength and splitting tensile strength of quaternary concretes.

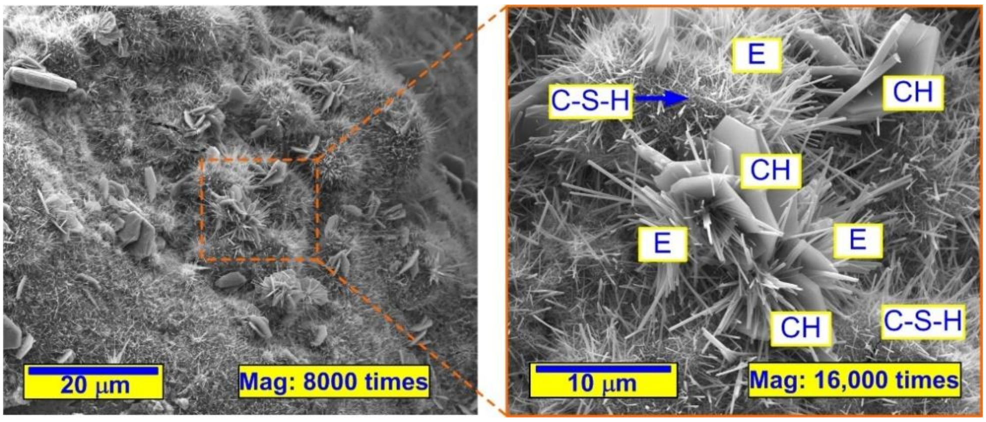
Mix	Analysed Parameters (MPa)	
	$f_{cm} \pm \delta$	$f_{ctm} \pm \delta$
REF	38.32 ± 1.74	2.90 ± 0.24
Q1	53.89 ± 2.61	4.02 ± 0.30
Q2	56.77 ± 3.36	4.26 ± 0.35
Q3	50.12 ± 4.52	3.76 ± 0.42

Analysis of convergence of the results obtained also allows to conclude that diversification of composition of the cement binder contributes to a slight increase in scatter of the obtained test results. The highest values of the standard deviation were observed for the Q3 series composite, i.e., at 30% substitution of the cement binder, and the smallest, on the other hand, in the reference concrete. Nevertheless, for every concrete, the level of variability in the results did not exceed 10%, which, however may indicate their convergence at an acceptable level, inclining to recognize the obtained average values of both strengths as fully reliable (Table 7). Satisfactory strength results obtained, both f_{cm} and f_{ctm} were tried to be explained by the accurate assessment of individual composite structures using SEM technology.

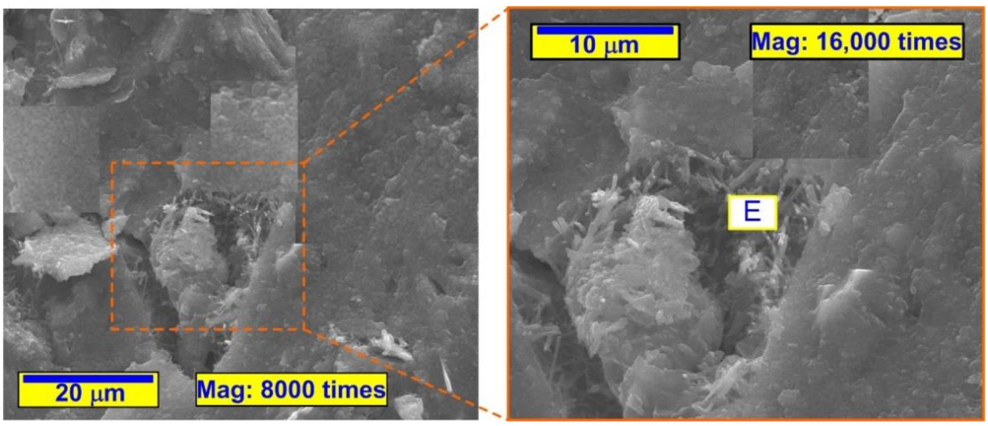
4.2. SEM Studies

Figure 3 shows sample representative SEM images of the microstructures of all the green quaternary concretes analyzed after 28 days of curing. Additionally, descriptions of characteristic details observed in the structure of all materials are summarized in Table 8.

From the inspection of the SEM images, a clear influence of the SCMs used can be observed, which caused a faster and more dynamic development of the cement matrix structure. There was a rapid growth of dense C-S-H phase in all quaternary concretes (Figure 3b–d), whereas, in the reference concrete, the stage of nucleation of individual types of phases was still visible (Figure 3a). The lack of the addition of pozzolanic-active and fine-grained supplements of OPC caused a significant delay in the formation of a dense matrix in the reference concrete. The structure of this composite was somewhat delayed in time, taking into account the curing processes of slurry, compared to the effects visible in the Q series concretes.



(**a**)



(**b**)

Figure 3. *Cont.*

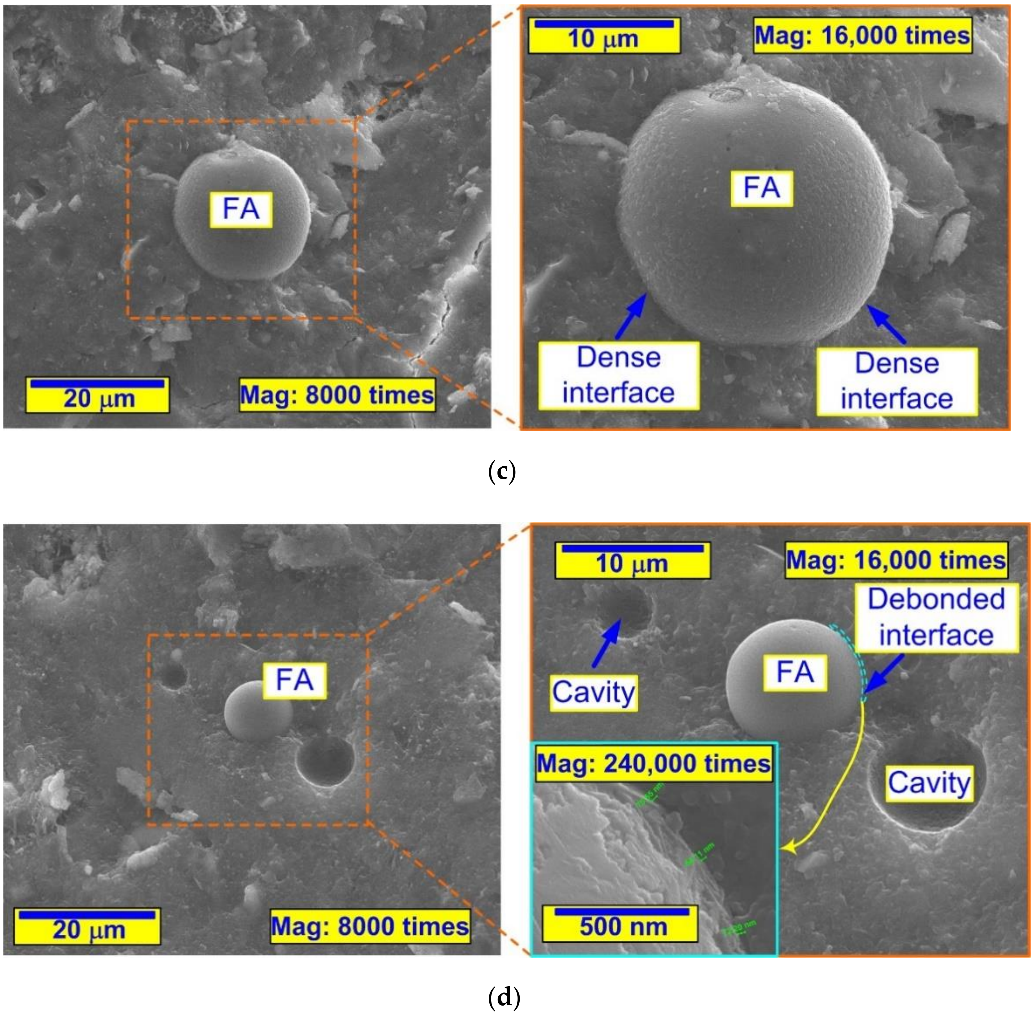


Figure 3. SEM micrographs of analyzed quaternary concretes including SCMs: (**a**) REF, (**b**) Q1, (**c**) Q2, (**d**) Q3; CH—calcium hydroxide, C-S-H—calcium silicate hydrate, E-ettringite, FA-fly ash.

In the quaternary concrete, with silica additives only, the structure contained a few porous places filled with ettringite phase products (Figure 3b). Composites containing FA were differed in structure, depending on the amount of waste used. In the concrete of the Q2 series, FA grains were well embedded in the matrix structure, and no visible damage was observed in the area of their contacts at the phase boundary. Concrete with a higher content of micro-filler, i.e., the Q3 series was characterized by a significantly worse morphology compared to the Q2 composite. A large amount of FA particles caused that they were not fully embedded in the structure of the matrix, and contained small microdamage in places of contact with the matrix. In numerous previous works, e.g., [98,155,157,162–164] it has been proven that a large amount of FA is not able to fully react during the formation of the matrix structure after 28 days of curing. The benefits of such a modification, however, are delayed with time. Thus, after a month, instead of strengthening it, one can, unfortunately, get the opposite effect.

This phenomenon, mentioned above, can be observed using magnification unprecedented for this type of material, i.e., 240,000 times. Thanks to this, it was possible to capture details and diagnosis of microcracks at the grain contact. One such magnification is presented in Figure 3d. In addition, in the concrete of the Q3 series numerous places with separated FA grains were observed. It can be concluded that the structure of this quaternary concrete presented in the SEM photographs is definitely the least favorable.

Table 8. Morphology of the matrix of analyzed quaternary concretes.

Mix	Morphological Characteristics of Cement Matrix (Based on Observations)
REF	• the first stages of phase nucleation in the material structure; • formation of the first phases structures in the composite; • diversification of all basic phases, matrix structure appears disordered; • the beginnings of the formation of the structures of CSH phase; • visible structures of the CSH phase in the form of needles; • visible of portlandite crystals.
Q1	• compact structures of the cement matrix with visible of CSH phase; • few pores visible in the matrix structure; • visible needles of the ettringite phase; • formation of phase structures comprehensively covering large areas of the matrix; • matrix structure appears to be highly homogenized; • the matrix structure is cohesive.
Q2	• compact structures of CSH phase; • the FA particles are bonded to the matrix; • the FA grains clearly "immersed" in the matrix structure; • the FA grains are faintly visible as they are embedded into the matrix structure and react; • increasingly compacted the matrix structure is visible; • compact interfacial transition zone between the FA grains and matrix.
Q3	• compact structures of CSH phase; • small visible defects at the boundary of the FA grains; • areas and cavities of separation of the FA grains from the matrix structure are visible; • reactive FA grains are visible; • weakly compacted interfacial transition zone between the FA grains and matrix; • the FA grains with ambivalent contact structure at junction with the matrix.

4.3. *Assessing of Environmental Benefits—CO_2 Reduction*

In addition to the benefits of improved mechanical parameters and structure of concrete as a result of the proposed modifications using several mineral additives, an analysis of the environmental benefits that may result from such a solution was also carried out. Table 9 presents the values of limitations in CO_2 emission generated during OPC production when replacing the main binder with individual compositions of SCMs.

Table 9. Annual reduction of CO_2 emission in green quaternary concrete with SCMs.

Mix	Annual Reduction of CO_2 Emission (ton)
REF	0
Q1	615,000,000
Q2	820,000,000
Q3	1,230,000,000

As a consequence, the production of concretes in which OPC would be replaced in the concrete mix with the proposed additives in particular percentage ranges could allow the significant reduction of CO_2 emissions in the range from over 0.6 mln tons to over 1,200,000,000 tons (Table 9).

When analyzing Table 9, it is clearly visible that the resulting environmental benefits are directly related to the percentage of materials used. The biggest limitation of CO_2 emission was obtained in the case of the Q3 series concrete, where OPC was replaced up to 30%. Reduction at the level of well over a million tonnes of CO_2 during the year is definitely not to be underestimated. In the case of the Q2 series composite, it will be possible to reduce CO_2 emission for nearly l million tons, when for the Q1 series concrete, only a little over 0.5 million tons.

5. Conclusions

The article presents the research results of basic mechanical properties and structures analysis of green concrete made on the basis of OPC and three pozzolanic active mineral additives. They were made using a basic additive currently used to modify the cement binder, i.e., FA, in two different proportions. In addition, non-compacted SF forms and modern nanoadditives in nS form were used. Research of mechanical parameters and microstructure of the subject composites were supported with environmental analyzes. The goal was to determine the tangible benefits of the applied modification of materials in the context of a possible limitation of CO_2 emission in the concrete industry, formed mainly in the process of Portland cement clinker burning out. (Figure 1). From the presented studies the following conclusions can be drawn:

(1) OPC substitution by each proposed composition of active pozzolan mineral additives brings measurable benefits in the results of the basic strength parameters of quaternary green concrete. The best results were obtained using the synergy of all three substitutes of the cement binder in the proportions used in the concrete of the Q2 series.
(2) The structure of the quaternary green concrete after 28 days of curing is characterized by a dense matrix. In the concrete of the Q1 series, porous places filled with transformation products of the ettringite phase were observed additionally. Concretes containing FA were characterized, however, by tight contacts in places of connection of grains with the matrix—in the case of a composite with a lower content of additive—and minor microdamage on the phase boundary, that were seen at a very high magnifications in the concrete with the addition 15% of FA.
(3) A small percentage of FA additive has a positive effect on the structure of the matrix containing a fine-grained and very active composition of additives in the form of SF and nS. Unfortunately, increasing the content of FA in the binder composition to over a dozen percent causes a clear weakening of the composite structure based on the quaternary binder.
(4) The structure of the reference concrete was disordered and has presented numerous phases during the process of their nucleation and transformation. This definitely translated into the weakest results of the mechanical parameters of this material.
(5) The results of the composites' mechanical properties testing show the highest convergence in the reference concrete. As the quantity of additives in the composition of the cement binder increases, the level of scatter of results increases. Nevertheless, it takes satisfactory values in all quaternary green concretes.
(6) Reducing the amount of OPC in the composition of the concrete mix in quaternary green concrete causes obvious environmental benefits associated with the significant reduction of CO_2 emission in the production of OPC from over 0.6 mln tons to over 1,200,000,000 tons.
(7) Quaternary green concrete containing additives and nanoadditives could be a useful alternative to plain concretes covering both the technical and environmental aspects.

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