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Zinc oxide as a functional admixture to cement composites

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Abstract: There is an increasing trend in the modern construction industry to use nanomaterials, which allow to improve the performance of construction materials on the one hand, and to shape new properties on the other. This study presents the results of physicomechanical and antibacterial tests for cement composites modified with zinc nanooxide. The main aim of this study was to compare the structural and morphological properties of three selected commercial zinc nanooxides and to determine the influence of the above mentioned nanooxides on the physicomechanical properties of cement composites and the ability to inhibit the activity of gram-positive and gram-negative bacteria as well as fungi. It was shown that commercial nanooxides can significantly differ in terms of physicochemical properties, which depend on their production method. Two of them were characterized by high specific surface areas, which in turn translated into rheological properties of cement mortars. Nanooxides with higher specific surface areas tend to reduce the plasticity of the mortars. According to the literature data, all nanooxides caused a delay in cement binder setting by more than 100%. This resulted in a reduction of the early one-day flexural and compressive strength of the composite. In the later curing period, especially after 7 days of hardening, a significant acceleration of the hydration process was observed in composites with the addition of all nanooxides, which was confirmed by significant increases in mechanical parameters. Nevertheless, the tested nanooxides showed different sensitivity towards microorganisms, which was influenced by both the type of nanooxide and bacteria.

Keywords: zinc oxide, admixtures, cement composites, antimicrobial tests

1. Introduction

Concrete structures are a wide field with inexhaustible possibilities for modification to improve their properties, which makes concrete more and more frequently and willingly used in construction in place of other construction materials such as brick, natural stone or wood. Thus, the production of cement is the second largest among all materials in the world. Up to now, cement clinker, and thus Portland cement, is the best binder used in concretes. Its reactivity is much higher than other components of common cements, with pozzolanic and/or hydraulic properties (Visali et al., 2021).

The performance of cementitious materials depends on structural constituents that are effective both at the micro and nano scale. The basic component responsible for the strength and other properties of cementitious materials is calcium silicate hydrate (C-S-H), the size of which is in the range of several nanometers. Therefore, the use of nanoparticles becomes advantageous, due to the wide possibility of improving mechanical and strength properties as well as unique features that result from their extremely small size (Liu et al., 2019). Nanoparticles are characterized by a size ranging from 1 to 100 nm, and their introduction into the cement matrix leads to its thickening and increases its compactness. In addition, nanoparticles characterized by a large BET surface area, are also characterized by high reactivity, which increases the pozzolanic reaction and the nucleation

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effect, accelerating the cement hydration process. This causes the consumption of calcium hydroxide so that more C-S-H phase is formed, increasing the strength of the cement composites. There are many types of nanoparticles, but the most common ones used in cementitious materials are nano-SiO_2, nano-Al_2O_3, nano-Fe_2O_3, nano-TiO_2, and nano-ZnO (Carmo et al., 2021).

Zinc oxide is a multifunctional material, characterized by piezo- and pyroelectric properties, a wide range of UV absorption and high photostability, biocompatibility and biodegradability. There are many methods of obtaining ZnO, including vapor deposition, hydrothermal synthesis, precipitation in water solution or from microemulsions, the sol-gel process and mechanochemical processes. The method of obtaining zinc oxide determines its properties, particle size and structure, which are the bases for a wide range of its application (Kołodziejczak-Radzimska and Jesionowski, 2014). ZnO nanomaterials are used in the supply of drugs, electronics, cosmetics, optics, thermal insulation dyes, photocatalytic degradation of organic pollutants and in the protection of steel bars against corrosion (Khalaf et al., 2021). Zinc oxide also has antibacterial properties (Shafeek et al., 2020; Klapiszewska et al., 2021). ZnO, nano-ZnO, zinc compounds, and all zinc-containing solids have been found to be effective in delaying cement hydration (Li et al., 2021). The mechanism of inhibition of cement early hydration is caused by the presence of Zn^{2+}, which can form low or impermeable layers of amorphous zinc hydroxide $Zn(OH)_2$ and crystalline calcium hydrocynite $CaZn_2(OH)_6 \cdot 2H_2O$ around the cement grains. The effect of this action is a delayed nucleation of the hydration product and prevention of the dissolving of cement. This leads to a supersaturation of calcium hydrate (C-H) and calcium silicate hydrate (C-S-H) in the solution, which accelerates the formation of the hydration and nucleation product in the subsequent hydration process. The discussed mechanism of zinc oxide action may adversely affect the mechanical strength of cement composites in the early stage of curing, and then significantly increase the mechanical properties over time (Wang and Aslani, 2021). The reason for the lower strength may be the detrimental effect of the hydration of the C_2S phase. Moreover, it was proven that hardened concrete containing ZnO is characterized by lower wettability, porosity and, consequently, reduced permeability compared to standard concrete (Kumar et al., 2021).

In this study, commercially available zinc oxides from Sigma-Aldrich, Chemat and Alfa-Aesar were compared. Their basic physicochemical parameters and antibacterial properties were assessed. The main purpose of the research was to use the analyzed zinc oxides as admixtures for cement mortars to determine their influence on the properties of fresh mortar (including the initial setting time, plasticity) and hardened mortar (including flexural and compressive strength, microstructure assessment). The final stage was the assessment of the antibacterial properties of the doped cement composites.

2. Materials and methods

As part of the research, commercially available zinc oxides were compared in terms of basic physicochemical and antibacterial properties and as admixtures for cement mortars.

2.1. Materials

Commercial zinc oxides from the following companies were used in the research: (*i*) Chemat, Gdańsk, Poland (ZnO-CH), (*ii*) Alfa-Aesar, Ward Hill, Massachusetts, USA (ZnO-AA) and (*iii*) Sigma-Aldrich, Saint Louis, Missouri, USA (ZnO-SA). In addition, CEM I 42.5R Portland cement (Górażdże S.A., Górażdże, Poland) and standard quartz sand (Kwarcmix, Tomaszów Mazowiecki, Poland) were used to produce cement composites.

2.2. Physicochemical and dispersive properties of zinc oxides

In order to compare and determine the dispersion properties of the used oxides, the samples were analyzed for particle size distribution using a Zetasizer Nano ZS device (Malvern Instruments Ltd., Malvern, UK). The apparatus uses the non-invasive back scatter technology (NIBS), which enables the examination of particle sizes in the range of 0.6-6000 nm.

In addition, as part of the publication, an analysis of the porous structure using a physisorption analyzer ASAP 2020 (Micromeritics Instruments Co., Norcross, Georgia, USA) was performed. The

porous structure parameters, such as BET surface area (A_{BET}), total pore volume (V_p) and average pore size (S_p), were determined in the framework of the study. The BET surface area was determined using the Brunauer-Emmett-Teller method, while the total volume and average pore size were determined according to the BJH (Barret-Joyner-Halenda) algorithm.

2.3. Preparation and testing methods of cement composites

In order to determine the influence of the used admixtures on the behavior and properties of the cement composite, the spread of the cement mortar was analyzed (using the flow table – see Fig. 1a) and the setting time of the slurry containing the analyzed admixtures was determined (using the Vicat apparatus – see Fig. 1b). Determination of the initial setting time of the cement paste containing the admixtures consisted of combining 500 g of cement with the amount of water selected in such a way that the distance between the Vicat bolt and the base plate was 6±2 mm in the cement mortar without the admixture placed in the apparatus ring. In the next step, the bolt was changed to a needle, and the initial setting time measurements were carried out until the distance between the needle and the base plate was 6±3 mm.

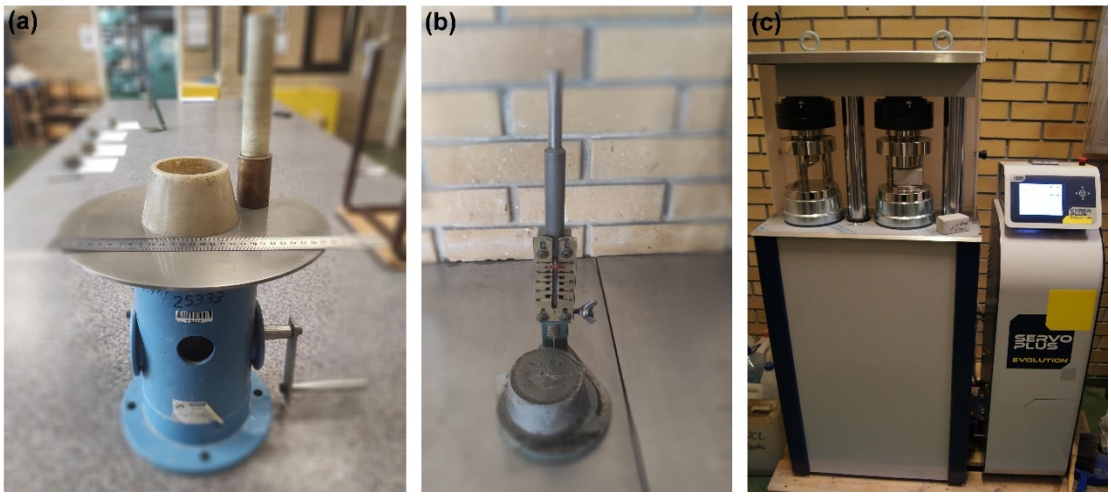

Fig. 1. Digital images of basic equipment used in the study: flow table (a), Vicat apparatus (b) and testing press machine (c)

In order to obtain a cement mortar, the appropriate amount of CEM I 42.5R Portland cement, standard quartz sand, water and the specified admixture in the amount of 0.1% of zinc oxide by weight was weighed or measured. The water/cement (w/c) ratio for mortars is 0.5, and sand/cement (s/c) is equal to 3. The cement was placed directly in the container of the mixer, while the introduced oxide was initially dispersed in water (forming a suspension with the use of a magnetic stirrer) and only then dosed into the container. The ingredients prepared in this way were mixed in accordance with the standard procedure EN 196-1. The prepared mortar was subjected to the test of the spreading value, which consisted of placing the tested mortar in a ring, in two layers, and then subjecting the system to 15 blows by turning the crank. After the shaking, the mortar cake was measured in two perpendicular directions. A similarly prepared cement mortar was placed in molds with dimensions of 40 mm x 40 mm x 160 mm and subjected to compaction (2 x 60 strokes). Subsequently, after 24 hours, the samples with a final curing time of 1, 7 and 28 days were disassembled. After the curing period, the specimens were subjected to flexural and compressive strength tests using the ServoPlus Evolution testing machine (Matest SpA, Treviolo BG, Italy) – see Fig. 1c.

Additionally, microstructural analysis of the obtained cement composites was carried out using the TESCAN3VEGA scanning electron microscope (Tescan, Brno, Czech Republic).

2.4. Microbial activity of pristine oxides and cement composites doped with ZnO admixtures

In addition, as part of the research, the microbial activity of the admixtures used was assessed by assessing the antimicrobial activity against selected colonies of gram-negative bacteria (*Pseudomonas*

putida, *Pseudomonas aeruginosa*, *Escherichia coli*), gram-positive bacteria (*Bacillus cereus*, *Staphylococos aureus*) and a member of fungi (*Candida albicans*). The final element of the application of the analyzed oxides is to use of them as admixtures to cement mortars as well as to assess the antimicrobial activity of the produced cement composites.

Each of the tested compounds (100 mg) was prepared in a 2 mL Eppendorf vial and sterile water was added. The samples were then shaken using a mini-shaker and a homogeneous suspension was obtained. Next, series of dilutions were carried out in order to obtain half of the previous concentration each time, which resulted in 8 suspensions. All solutions were stored in a refrigerator at 4 °C for no longer than a week.

Culture of each species was transferred from agar plates into 20 mL 50% TSB broth (Sigma Aldrich, Saint Louis, Missouri, USA). Then, each of the cultures was incubated for 24 hours at 30 °C. When the cell suspension reached optical density equal to approx. OD_{600} = 0.1, which corresponds to 10^6 cells per millilitre, the biomass was diluted (1:50) to give 2×10^4 cells per millilitre.

The antimicrobial activity test was carried out in accordance with the European Committee on Antimicrobial Susceptibility Testing, using the micro-dilution method according to the EUCAST guidelines. In a sterile 96-well plate, 50 µL suspensions of each dilution were placed from the highest to the lowest dilution, starting form the first row of the plate. Subsequently, 200 µL of microorganisms suspension (2×10^4 CFU per mL) with resazurin (4 mL of dilution at 0.5 mg/mL added to 20 mL of microbial suspension) were added. The concentrations ranged from 0.157 to 20 g/L (0.157, 0.315, 0.63, 1.26, 2.52, 5, 10, 20 g/L). The microorganisms with resazurin but without the analyzed compounds (biotic control) as well as the compound solutions with resazurin lacking microorganisms (abiotic control) were used as controls.

Three replications were prepared for each of the tested compounds. Plates were then incubated at 30 °C for 24 hours, with constant stirring on a rocker shaker, after which the results of MIC (the minimal inhibition concentration) and MBC (the minimal bacterial concentration) or MFC (the minimal fungal concentration) were obtained.

3. Results and discussion

3.1. Physicochemical and dispersive properties of zinc oxides

In order to characterize the properties of the used ZnO powders, an analysis of the particle size distribution was performed, which allowed to observe the material's tendency to aggregate and agglomerate. In addition, an analysis of the porous structure was performed, which allowed to determine the most important structural parameters. The conducted analyzes allowed to accurately distinguish the nature of the used powder materials. The results of the performed analyzes are summarized in Table 1.

The particle size distribution data for the individual oxides varied significantly, resulting in some variation between the products. ZnO-AA product is characterized the largest particle size distribution in the range 142-6439 nm. Such large differences in particle sizes are confirmed by the highest polydispersity index, which is equal to 0.446. ZnO-CH and ZnO-SA materials, with particle sizes in the ranges of 255-825 nm and 142-531 nm, are characterized by significantly lower particle size distribution. These oxides are characterized by a similar polydispersity index, which is equal to 0.054 for the ZnO-CH material, and 0.052 for ZnO-SA. As part of our work, the particle size distribution was measured in isopropanol. As demonstrated by the authors of the work (Vinardell et al., 2017), the environment in which the measurements are carried out is of fundamental importance, therefore the obtained values may differ from those declared by the producers. This has been demonstrated by the research carried out by scientists on the particle size distribution of zinc oxides with the declared values of 50 and 100 nm in three different measurement environments: distilled water, phosphate buffered saline (PBS) and Dulbecco's modified Eagle medium (DMEM). Each of the conducted analyzes achieved different results. It was shown that the particles in distilled water and PBS solutions exhibited the greatest tendency to aggregate, while particles in DMEM had the lowest tendency. Similarly, the highest PDI index values were obtained after carrying out the measurements in the PBS

solution. The PDI value of 0.3 was achieved for the analyzes performed in distilled water and DMEM solution.

In the case of the results obtained during the analysis of the porous structure, the material with the most developed BET surface area value equal to 17.5 m^2/g is ZnO-AA. Slightly lower values of this parameter were determined for the ZnO-SA product (12.5 m^2/g), and the lowest value was observed for the ZnO-CH sample for which A_{BET} is equal to 4.8 m^2/g. After a comparison of the obtained total pore volume data, it was again observed that the ZnO-AA product is the material with the highest value of this parameter, reaching 0.0062 cm^3/g. A slightly lower value was obtained for the zinc oxide from Sigma-Aldrich, equal to 0.0047 cm^3/g, and the lowest total pore volume (0.0019 cm^3/g) was obtained for the material from the Chemat company. A similar relationship was observed after an analysis of the average pore size results for the discussed zinc oxides. In order of decreasing values, the following values were obtained: 2.20 nm (ZnO-AA), 2.19 nm (ZnO-SA) and 2.18 nm (ZnO-CH). Analyzing the available literature data, in the work of Barahuie and coworkers (Barahuie et al., 2014), scientists conducted a study of the porous structure reaching the BET surface area parameter equal to 6.0 m^2/g, BJH pore volume - 0.03 cm^3/g and BJH average diameter parameter equal to 4.0 nm. In turn, Thejaswini and colleagues (Thejaswini et al., 2016) analyzed the parameters of the porous structure of zinc oxide and obtained a BET surface area of 13.5 m^2/g, a pore volume of 0.06 cm^2/g and a micro-pore radius of 1.22 nm. Similar parameters were achieved by Ama and Arotiba (Ama and Arotiba, 2017) using a synthesized zinc oxide. The BET surface area determined by the scientists was equal to 8.3 m^2/g, and the pore volume was at 0.0562 cm^3/g. Based on the data presented above, it can be concluded that the methodology of obtaining zinc oxide has an impact on the obtained values of the porous structure, but the differences are not significant.

Table 1. Dispersive and porous structure properties of zinc oxides used in this study

Sample	Dispersive properties		Porous structure properties		
	Particle size range (nm)	Polydispersity index	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore size (nm)
ZnO-CH	255-825	0.054	4.8	0.0019	2.18
ZnO-AA	142-6439	0.446	17.5	0.0062	2.20
ZnO-SA	142-531	0.052	12.5	0.0047	2.19

3.2. Analysis of cement composites

The analysis of cement mortars began with determining the plasticity and initial setting time of fresh cement mortars. The results of the analyzes are presented in Fig. 2, additionally in Fig. 3 there are digital images of mortars without the admixture and doped with zinc oxides during the plasticity test.

The plasticity test, apart from the zinc oxide doped mortars, was also carried out for the pure mortar as a reference sample, which reached a flow value of 17.0 cm. The same spreading value was achieved by the mortar containing the ZnO-CH admixture, it is also the highest spreading value achieved by the zinc oxide doped mortar. Slightly lower spread (16.5 cm) was achieved for the mortar containing an admixture of the ZnO-SA material. The lowest value of the flow was obtained for the ZnO-AA product, which was equal to 16.0 cm. The influence of the admixture on the plasticity of the cement paste was presented in the work Liu and coworkers (Liu et al., 2019). They confirmed that with the increase in the content of zinc oxide admixture in the slurry, the diameter of the obtained flow slightly decreased.

By analyzing the effect of introducing zinc oxide admixtures into the cement matrix, the initial setting time parameter was determined. For the reference sample, without any admixture, the initial setting time began after 170 min. Zinc oxide admixtures caused quite a significant delay in setting the cement matrix. For the ZnO-AA material, the initial setting time was determined after 385 min, which is the shortest value among the used zinc oxides. The mortar with ZnO-CH admixture needed a slightly longer time to start cross-linking of the cement matrix (410 min). The admixture that caused the greatest extension of this time is the ZnO-SA material, the initial setting time is set here after 460 min.

Zinc oxide has been used previously as a setting delay admixture, as demonstrated in the work by Liu and coworkers (Liu et al., 2019). Scientists showed that ZnO delays cement hydration by forming a crystalline layer at the start of the produced hydration products. In their research, they also proved that the addition of zinc nanooxide inhibits the hydration of C_3S and C_2S phases in the cement slurry, prolonging the induction period.

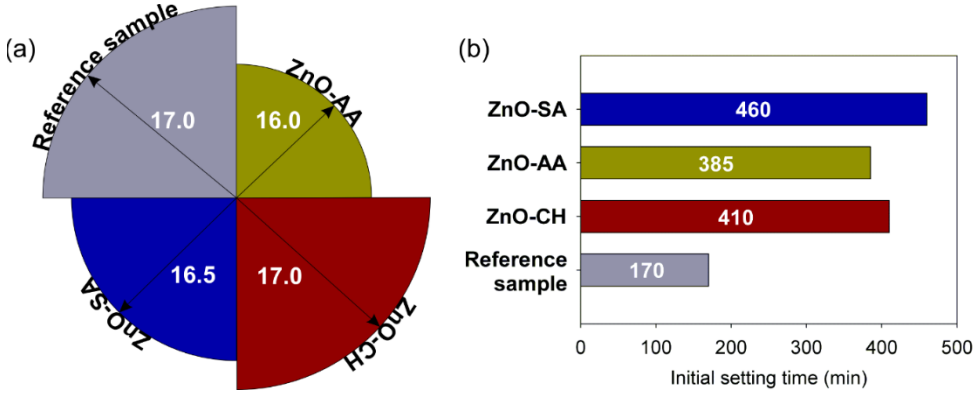

Fig. 2. Plasticity (a) and the initial setting time (b) of mortars

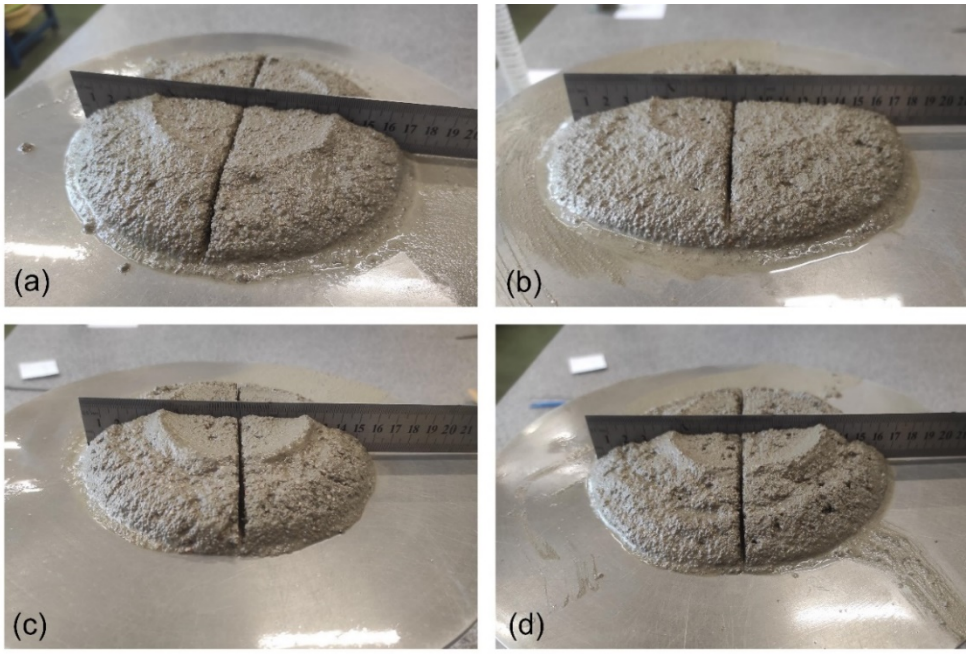

Fig. 3. Digital images of cement mortars during plasticity testing without (a) and with ZnO-CH (b), ZnO-AA (c) and ZnO-SA (d) admixtures

After determining the properties of the fresh mortar, the influence of the applied admixtures on the mechanical properties was checked. For this purpose, the produced cement mortar samples were tested for flexural and compressive strength after 1, 7 and 28 days of curing. The results of the analyzes are presented in Fig. 4 and additionally digital images taken during and after the strength tests are presented in Fig. 5.

The obtained flexural strength results confirm that the admixture of zinc oxide delays the setting time of the cement mortar. This is evidenced by the higher average flexural strength after 1 day for pure mortar compared to mortars doped with zinc oxides. After 7 days, the positive effect of the introduced admixtures in all the types of used zinc oxide can be observed. The full flexural strength was determined for the samples after 28 days of curing. The value of 9.4 MPa was obtained for the reference sample, while the doped sample with the highest flexural strength value is ZnO-CH (9.6

MPa), and the samples with slightly lower strength values, compared to the reference sample, are mortars with ZnO-AA (9.1 MPa) and ZnO-SA (9.1 MPa).

Taking into account the results obtained from the compressive strength analysis presented in Fig. 4b, the similar nature of all analyzed samples was confirmed. As in the case of flexural strength, the delaying nature of the zinc oxide admixture is noticeable, which completely changes after 7 days of maturation. When analyzing the full strength of the mortars after 28 days of curing, it was noticed that the reference sample reached the strength equal to 63.1 MPa. All samples doped with ZnO oxides are characterized by higher strength, especially after 7 days of curing. For the ZnO-SA sample, the strength increase by 1% was achieved, while the ZnO-CH-doped mortar was characterized by the value of the compressive strength higher by 3%. The composite with the highest difference in strength compared to the reference sample is the ZnO-AA material with a value higher by 4%. It is noteworthy that there is little difference between 7 and 28 days compressive strength for mortars with zinc nanooxide additives compared to pure mortar. The smallest differences were obtained for ZnO-CH. This is due to the fact that the cement used is CEM I 42.5R with fast strength increase in the initial period of hardening, reaching almost 70% of the 28-day strength already after 2 days. It is a cement that contains large amounts of C_3S phase, which is responsible for setting the cement binder in the first period of hardening. The use of zinc nanooxides additionally accelerates the hydration of the cement binder by introducing into the structure of the cement matrix additional active centers, from which the growth of the C-S-H phase begins. This is also due to the so-called "filling effect". Nano-additives initially physically thicken the structure of the cement matrix, reduce its porosity and thus increase the adhesion of the cement paste to aggregate, resulting in an increase in the strength of the mortar. The differences in the nanooxides used, the best results for ZnO-CH, are also due to the tendency of individual nanooxides to aggregate and agglomerate. Of the three oxides tested, the ZnO-CH oxide showed the least particle aggregation, which probably resulted in better distribution in the cement matrix and increased its efficiency.

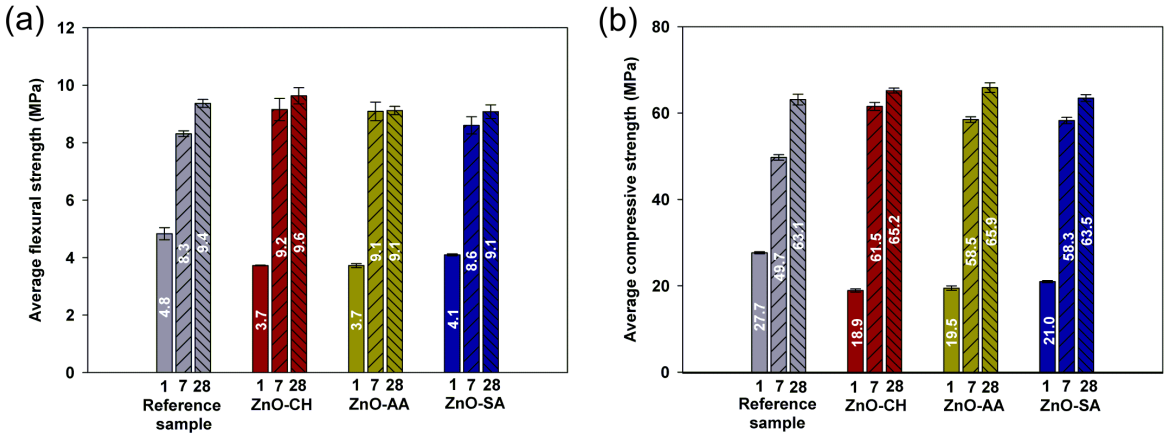

Fig. 4. Average flexural (a) and compressive (b) strength of cement mortars after 1, 7 and 28 days maturation

The beneficial effect of zinc oxide on the mechanical properties of cement mortars was also confirmed in their research by Nochaiya and coworkers (Nochaiya et al., 2015). They assessed the influence of 1, 2 and 5 wt% admixture on the cement mortar. In another work, Nivethitha and Dharmar (Nivethitha and Dharmar, 2016) also confirmed the beneficial effect of 1, 3 and 5 wt% admixture of this oxide on compressive strength and split tensile strength.

In order to illustrate the differences between the produced cement mortars, after 28 days of curing, SEM pictures of the analyzed cement matrices were taken, which are shown in Fig. 6. The presented SEM pictures clearly show the different nature of the obtained cement composites caused by differences related to a different type of zinc oxide used. However, the effect of all the zinc oxides used in sealing the structure of the cement composite, resulting from the analysis of the SEM images, is worth noting. Also, the authors of the works (Nazari and Riahi, 2011; Nochaiya et al., 2015; Liu et al., 2019) demonstrated the compaction and sealing of the structure of a cement composite containing an admixture of zinc oxide in their research.

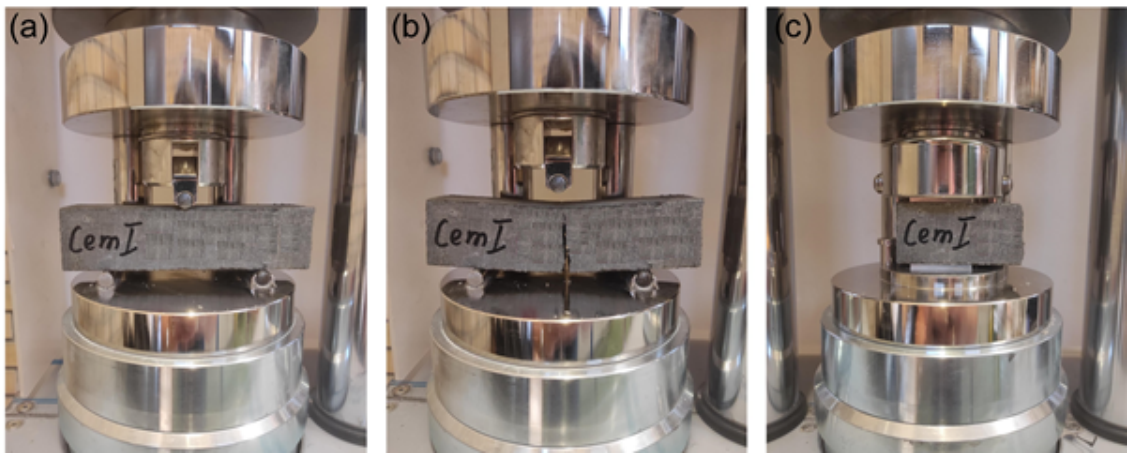

Fig. 5. Digital images of cement mortar during (a) and after (b) flexural strength test and sample during compressive strength test (c)

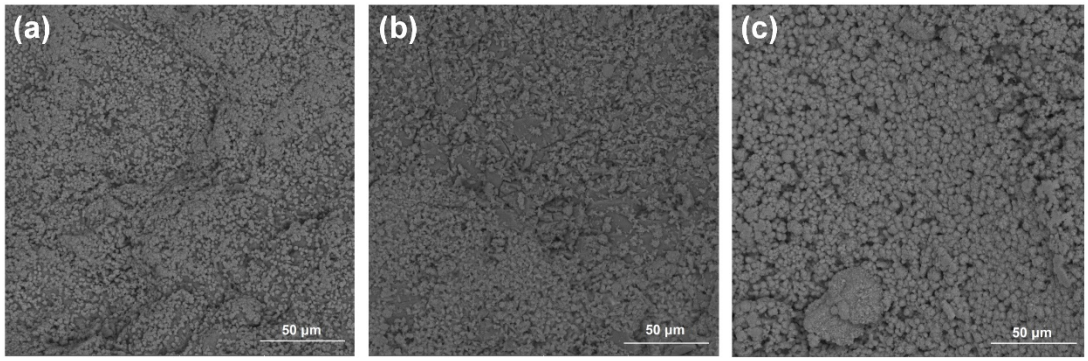

Fig. 6. SEM images of cement composites doped with ZnO-CH (a), ZnO-AA (b) and ZnO-SA (c)

3.3. Antibacterial tests

The testing of antibacterial properties of the studied materials included two stages – preliminary evaluation of microbial purity and subsequent determination of growth inhibition expressed as MIC (minimal inhibitory concentration) and MBC/MFC (minimal bactericidal/fungicidal concentration).

The results of microbial purity tests were presented in Table 2 and Fig. 7. The obtained results indicate that the antimicrobial properties of the tested samples vary depending on the material used. The best results were obtained for ZnO-SA, in case of which there was no visible microbial growth. Visual inspection of Petri dishes with the ZnO-AA sample revealed the presence of single colonies under the sample. Sample ZnO-CH was characterized by the lowest microbial purity, which is visible in Fig. 7 as a yellow growth which spreads in all directions for beneath the sample. In this case the microbial growth was similar to that which occurred in case of pure cement which was used as a reference sample.

The second stage of the studies was focused on the determination of MIC and MBC/MFC values towards commonly tested bacterial and fungal species (see Table 3 and Table 4). The analysed range of concentrations was equal to 0.156–20 g/L. The lowest MBC/MFC as well as MIC values (which

Table 2. Microbial purity results

Sample	Observations
ZnO-CH	Extensive microbial growth under the sample
ZnO-AA	Single colonies under the sample
ZnO-SA	Lack of microbial growth

correspond to the highest antimicrobial effect) were obtained in case of ZnO-SA, followed by ZnO-AA, whereas the values for ZnO-CH were notably higher in most cases. The parameters were also species-dependant. Among the studied microorganisms, *E. coli* was the most susceptible to the antimicrobial effect of the studied materials (MIC at 1.25 g/L; MBC at 5 g/L), whereas *P. putida* exhibited the highest resistance among the studied microorganisms (MIC at 20 g/L; MBC at >20 g/L). It should be noted that in case of ZnO-SA the MIC and MFC against *C. albicans* are also low, which indicates high antifungal potential of this material.

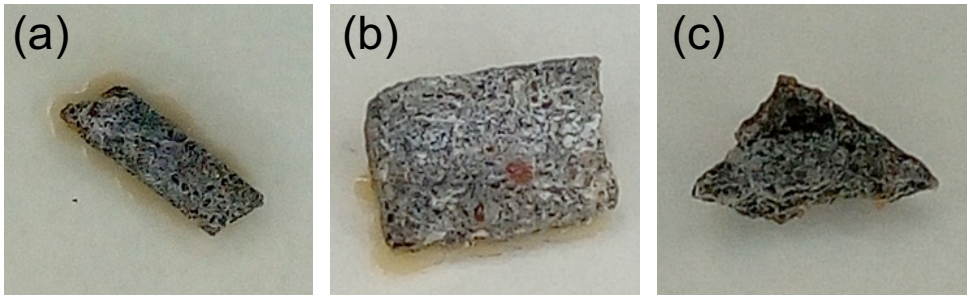

Fig. 7. Digital images of ZnO-CH (a), ZnO-AA (b) and ZnO-SA (c) cement mortar samples subjected to microbial purity tests

Table 3. Evaluation of microbial activity of gram-negative bacteria of the studied materials

Sample	*Pseudomonas putida* G-		*Pseudomonas aeruginosa* G-		*Escherichia coli* G-	
	MIC *	MBC *	MIC *	MBC *	MIC *	MBC *
ZnO-CH	20	Above 20	20	Above 20	5	20
ZnO-AA	20	Above 20	20	Above 20	1.25	5
ZnO-SA	20	Above 20	10	Above 20	1.25	5
Pure cement	Above 20	Above 20	Above 20	Above 20	Above 20	Above 20

* data presented in g/L unit

Table 4. Evaluation of microbial activity of gram-positive bacteria and fungal species of the studied materials

Sample	*Bacillus cereus* G+		*Staphylococcus aureus* G+		*Candida albicans* yeast	
	MIC *	MBC *	MIC *	MBC *	MIC *	MFC *
ZnO-CH	20	Above 20	Above 20	Above 20	Above 20	Above 20
ZnO-AA	10	Above 20	20	Above 20	10	Above 20
ZnO-SA	10	Above 20	20	Above 20	5	Above 20
Pure cement	Above 20	Above 20	Above 20	Above 20	Above 20	Above 20

* data presented in g/L unit

Zinc oxide has been recognized as a material with confirmed antimicrobial activity and its potential application in numerous sectors of the industry has been an object of several studies (Ijaz et al., 2020; Jin and Jin, 2021). Research regarding the use of zinc nanoparticles as antimicrobial additives has been focused on e.g. wound healing (Jin and Jin, 2019), supplementation of animal feed (Mohd Yusof et al., 2019), food packing (de Azeredo, 2013), prevention of dental infections (Jiang et al., 2020), construction materials with antifungal properties (Zeng et al., 2016) as well as clean surface materials for areas which require a sterile environment (e.g. hospitals or nurseries) (Sikora et al., 2017).

Based on the current state-of-the-art knowledge, the ability of zinc oxide nanoparticles to effectively inhibit microbial growth may be associated with several different phenomena. The interaction between the nanoparticles may either be direct or indirect. The first scenario assumes a direct contact between zinc oxide particles and cellular membranes, which results in the disruption of the latter (Sirelkhatim et al., 2015). The second, indirect scenario is based on the generation of

intermediates by zinc oxide, which then interact with the cells with lethal effects. In this case, the possible mechanisms include generation of reactive oxygen species (Dwivedi et al., 2014) or active zinc cations (Pasquet et al., 2014), which are responsible for the antibacterial effects. Damage to the membranes resulting from a direct reaction with nanoparticles or the intermediates would destabilize the cellular transport processes and cause malfunction/termination of basic biological cycles. This is often evidenced by the release of crucial cellular building-block compounds (e.g. proteins and/or nucleic acids) for cells (Reddy et al., 2014).

Taking into account the multiple possible mechanisms of action, the antimicrobial properties of ZnO may differ depending on the concentration, species of microorganisms, exposure time and environmental conditions (Lallo da Silva et al., 2019). However, it has also been implied that the toxicity of ZnO towards microorganisms may also be affected by its morphology (Talebian et al., 2013), which is associated with its synthesis method. Indeed, the quality of precursor materials, the procedure used for their treatment, the solvents, pH and temperature have a significant impact on the size and shape of ZnO particles. This correlation corresponds well with the findings presented in the framework of this study, as various antimicrobial effects were observed for the studied ZnO samples which were obtained from different sources and characterized by different morphology. The structural differences may affect the modes of interaction described above, as the morphology of nanoparticles would notably influence the possibility to directly affect the cells and modulate the amount of active sites for reactive oxygen species generation or release of zinc cations. The obtained results elucidate the necessity to conduct a detailed morphological analysis of zinc oxides in order to achieve uniform and repeatable antimicrobial effects and may potentially explain the different effects observed against the same microbial species under similar testing conditions.

In case of zinc oxides investigated in the framework of this study, we assume that the morphological and microstructural differences which most likely occurred as a result of different synthesis methods, were responsible for the observed differences in terms of antimicrobial activity. Even the presence or absence of slight structural defects (e.g. cracks) may notably affect this property by increasing or decreasing the amount of active for radical generation, while the disruption of the crystal lattice of ZnO may facilitate the release of zinc ions. Most likely, this is the basis for the notable difference between the ability of ZnO-SA and ZnO-CH to inhibit microbial growth, however subsequent research is needed to provide adequate rationale.

Future studies should focus on establishing the optimal morphological properties of ZnO nanoparticles in terms of their antimicrobial properties based on an extended number of samples. An in-depth analysis of structure-properties with regard to direct and indirect mechanisms of interaction is also a priority. The use of additives to zinc oxides as means of improving the antimicrobial effect (Klapiszewska et al., 2021) is also a desirable path for further improvement.

4. Conclusions

As part of the research, three commercial zinc oxides were used as functional admixtures for cement mortar. The zinc oxides used were characterized by defined dispersion properties and a porous structure. Each of the used oxides tends to form larger aggregates and agglomerates. In addition, the used oxides are characterized by a comparable size of the BET surface area, which, depending on the product, is in the range of 4.8-17.5 m^2/g and pore sizes in the range of 2.18-2.20 nm.

Cement composites produced with the use of zinc oxides were characterized, depending on the material, by comparable (ZnO-CH) or lower (ZnO-AA and ZnO-SA) plasticity in relation to the reference sample. The applied zinc oxide admixtures increased the initial setting time of the cement slurry. The mortar containing ZnO-AA admixture was characterized by the shortest time among the doped mortars (385 min), while the ZnO-SA material was characterized by the longest (460 min).

Each of the used zinc oxides, in spite of the lower early strength associated with the delay in setting of the cement composite, achieved favourable strength values. In the case of flexural strength, these values are very similar to those obtained for the reference sample. Compressive strength for all doped mortars was higher than the reference sample. The highest compressive strength value after 28 days of curing was achieved by the ZnO-AA sample (65.9 MPa).

Based on the analysis of SEM images of the microstructure of cement composites, compaction and sealing of the structure of the final products were observed.

The admixtures used were also characterized by defined antibacterial properties against gram-positive and gram-negative bacteria. The highest antimicrobial activity was obtained for ZnO-SA, then ZnO-AA, while ZnO-CH is characterized by the lowest antimicrobial effectiveness. The species of the analysed microorganisms also influenced the obtained results. *E. coli* bacteria were the most susceptible to antimicrobial activity, while *P. putida* showed the highest resistance. In relation to *C. albicans*, ZnO-SA material has the highest antifungal potential.

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