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Effect of Surface Hydrophobization on the Durability of Concrete with Cement Kiln Dust

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ABSTRACT

The examinations of concrete involved partial substitution of cement with cement kiln dust (CKD) 0, 5, 10, 20 and 30%. The water/cement (w/c) ratio amounted to 0.36. The obtained findings pertaining to open porosity, density, and volumetric density were found to correlate with the capillary action and absorptivity of the analyzed types of concrete. With the maximum addition of CKD, i.e. 30%, open porosity decreased by 35%. In turn, CKD added in the amount of 5% resulted in a slightly reduced addition compressive strength, amounting to 1.3% and 2.1% following 28 days and 56 days of concrete curing, respectively. After 28 days, the differences in strength were greater when the additive was supplied in higher amounts, i.e. 10%, 20%, and 30%, resulting in 6.5%, 13.4%, and 22.9% decrease, respectively, in spite of strength improvement. In terms of flexural and splitting tensile strengths, comparable relations were noted. As far as the frost resistance test results are concerned, the mass losses in all examined concretes were not significant, reaching up to 0.5%. The strength reduction in the case of the first three series of concretes was below 3%. When the CKD addition was increased to 20% and 30%, the value of the dynamic modulus of elasticity $E_{c,s}$ decreased to a greater degree, by 8.0% and 14.7%, respectively. The hydrophobization effect is best seen in CKD-free concrete. After the impregnation, the loss of mass following the frost test of the samples is reduced by half. With a higher CKD content, the hydrophobization effectiveness is insignificant. The most favourable results were observed for hydrophobization with the oligomer-based preparation A1.

Keywords: concrete, cement kiln dust, hydrophobization, frost resistance, salt crystallization.

INTRODUCTION

According to key statistics, global cement production in 2022 is estimated at 4.1 billion tons. Considering the figures for 2012 (3.7 billion tons), this figure increased by 400 million tons in 10 years of development in the construction industry. The largest cement producers are China, producing 2.1 billion tons of cement annually, India producing 370 million tons of cement, Vietnam –120 million tons and the US – 95 million tons of cement [1]. The technological process of cement production involves the emission of dust and greenhouse gases into the atmosphere (GHGs), energy consumption, environmental pollution, water consumption, waste generation and land degradation [2]. According to Miller et al. [3], the cement industry contributes approximately 7% of greenhouse gas pollution in the atmosphere each year. Most greenhouse gases are emitted in the course of the pure clinker production, which is needed to make cement. Since pure

CEM I portland cement should contain at least 95% clinker [4], cement plants are increasingly abandoning portland cement production in favor of cements with more additives, i.e. blast furnace slag and fly ash. The use of mineral additives in concrete technology decreases the consumption and cost of cement, as well as modifies and shapes the properties of mortars, cement pastes, concretes and plasters [5, 6, 7].

A by-product of cement production is cement kiln dust (CKD) extracted at the kiln firing plant. It is estimated that industrial cement is the second largest emitter of mineral dust, following the power industry. According to key statistics, they collectively account for 15 to 20% of the cement produced [8]. Dusts not only have a harmful effect on human health but can infiltrate into the soil and groundwater, polluting them. The chemicals present in cement dust can change the pH of the soil and have harmful effects on plants and water-dwelling organisms. Faced with such a high environmental impact, the cement industry is striving worldwide to reduce environmental pollution while cutting costs. The use of modern solutions in cement plants, i.e. the change in firing technology (dry instead of wet) and the installation of dust-capturing equipment have made it possible to reduce dust emissions into the atmosphere. Owing to the use of electrostatic precipitators, bag filters or pulse dust collectors, dusts are captured and, in the case of a suitable composition (dusts that do not contain alkali, heavy metal chlorides or sulfates), reused for cement production [9, 10]. This reduces the consumption of clinker. In many countries, the dust gathered in dust collectors is reused in cement production, unfortunately often preceded by storage in cement plants. CKD is classified as non-hazardous solid waste. The growing volume of waste also creates problems related to the need for disposal and the growing need for storage space. Therefore, it is important to reprocess waste to ensure sustainability.

The dust composition is dependent upon the raw material quality, the technology of production, fuel type and the method of dust removal. Dusts consist of clinker-derived dust, unreacted raw material components, as well as ash from halides, sulfate-containing fuels and also volatile organic compounds (VOC). Siddique [11] observed a higher proportion of calcium in the dusts formed during the dry process as opposed to the dusts from wet processes. Adaska and Taubert [12], on the other hand, observed a higher amount of K_2O in the dusts formed in fuel oil- or gas-fired kilns compared to coal-fired kilns. The reactivity of cement dusts is influenced by the proportion of free calcium CaO (about 30–40%) and losses on ignition (LOI) [13, 14, 15]. CKD is currently used in environmental protection for neutralization of acidic wastewater [16, 17], water purification [18, 19], liming and fertilization of soils [20], stabilization and hygienization of hazardous waste [21]. Due to its high content of free calcium, CKD has binding properties and can be successfully used in soil stabilization to replace lime, fly ash or portland cement [14, 22]. In the construction industry, CKD is used to partially or fully substitute cement, as a filler in mineral and asphalt mixtures for the manufacturing of controlled low-strength construction materials (CLSM) as [23]. El-Sayed et al. [24] used CKD to produce lightweight cement composites with liquefied polystyrene (LPS) with acoustic and insulating properties. As a result of the high SiO_2 and Al_2O_3 content in CKD, this waste can become a silica precursor for the synthesis of porous aluminosilicate nanomaterials used in nanotechnology, i.e. imogolite and allophane [25, 26, 27, 28]. The literature contains many examples of cement dust applications in concrete technology, both as an additive to cement and as a replacement [24, 29, 30]. There is a general trend of a reduction in density as well as improvement in porosity, weight and capillary absorption with an increase in the amount of CKD in cementitious slurries, mortars and concretes [11, 31]. In the case of strength parameters, CKD used as a cement replacement above 5% decreases the tensile and compressive strengths of portland cement concretes [11], as observed in studies [32–35], the addition of up to 5% dust does not significantly decrease the durability and mechanical properties of the materials tested. Additionally, excessive CKD addition can adversely affect the corrosion of concrete strengthening and the susceptibility of the grout to the negative effects of alkaline reaction of the aggregate resulting from an increased alkali content of the cement slurry. Better results were achieved when CKD was used in the concretes with pozzolanic additives, slag cement or special sulfate-resistant cement. Many authors [36, 37] have observed enhanced flexural splitting, splitting tensile and compressive strengths with the simultaneous use of an optimal amount of CKD (up to 10%) as well as fly ash and granulated blast furnace slag and as additives. The important role of CKD in activating the properties of pozzolanic additives during cement hydration as well as the increase in ettringite volume was found. It has also been observed that the use of pozzolanic additives can reduce the negative effect of the alkaline reaction occurring during the use of CKD in concretes [31]. Abdelgader et al. [38] investigated the impact of slag coal ash – used as a cement substitute – on the grout rheology as well as the influence on the final concrete properties. They showed that slag coal ash constitute prospective industrial by-products which can effectively replace cement without sacrificing strength development and workability. The continuous development of technology and recent years of research show the great potential of CKD not only in the environmental, agricultural or geotechnical industries but especially in the construction sector. This paper demonstrates the findings of testing concretes with different amounts of CKD 5, 10, 20, 30% as a cement substitute and the effectiveness of their surface hydrophobization with siloxane and methyl silicone resin. The mechanical and physical properties of the non-hydrophobized concretes as well as the dynamic and static modulus of elasticity after cyclic freezing-thawing and frost resistance were determined. Subsequently, the effectiveness of hydrophobization was determined by testing the weight absorption, capillary absorption, resistance to salt crystallization and frost-resistance of modified concretes. Taking into account the fact that the composition of dust and, consequently, the properties of the material with CKD differ among various cement plants, it becomes fully justified to continue research on the properties of building materials with this material.

MATERIALS AND METHODS

Materials

In-house tests were performed by introducing the addition of CKD via partial substitution of cement. Table 1 shows the concrete mixtures compositions. In all the concretes, the water/binder (w/b) ratio was 0.36. The main binder employed in the study was CEM I 42.5R portland cement (Cemex Poland) that was tested according to the PN-EN 197-1:2012 standards [4]. The chemical composition of cement is as follows: CaO (64.41%), SiO_2 (20.23%), Al_2O_3 (3.62%), Fe_2O_3 (4.36%), MgO (1.36%), Na_2O (0.26%), K_2O (0.55%), Na_2O_{eq} (0.63%).

Its basic physical parameters are introduced in Table 2. The concrete was prepared using natural gravel and rinsed quartz sand. The aggregates were characterized by a density of 2.65 kg/dm^3. Polycarboxylate superplasticizer was applied as chemical admixture. The chemical composition of the CKD from a Polish cement production plant is as follows: CaO (41.1%), SiO_2 (8.7%), Al_2O_3 (2.8%), Fe_2O_3 (1.3%), MgO (1.2%), Na_2O (0.7%), K_2O (30.5%), Cl (6.7%), LOI (6.61%; LOI, loss on ignition (no data)). The physical properties of CKD are as follows: bulk volume 560 kg/m^3, specific gravity 2.67 g/cm^3, specific surface area 6000 cm^2/g, maximum particle size 0.30 mm, and gradation 0.03 mm. Figure 1 shows CKD in 20,000× magnification; visible grainy structure of the dust can be observed. The visible particles can be identified as agglomerations of small dust grains; it can be seen that some of them adhere to larger particles. It can be noted that the

Table 1. Composition of concrete mixtures

Specimen	Cement	CKD	CKD	Superplasticizer	Sand	Aggregate 2/8 mm	Aggregate 8/16 mm	Water
	(kg/m^3)	(kg/m^3)	%	(kg/m^3)	(kg/m^3)	(kg/m^3)	(kg/m^3)	(dm^3/m^3)
C0	385.00	0	0	1.9	468.1	635.6	635.6	138.6
C5	365.75	19.25	5					
C10	346.50	38.50	10					
C20	308.00	77.00	20					
C30	269.50	115.50	30					

Table 2. Physical properties of the CEM I 42.5 R cement

Soundness (Le Chatelier) mm	Specific surface (cm^2/g)	Specific gravity (g/cm)^3	Initial setting time (min)	Heat of hydration (J/g)	2-days compressive strength f_c (MPa)	28-days compressive strength f_c (MPa)
0.8	4049	3.07	190	306	31.0	60.5

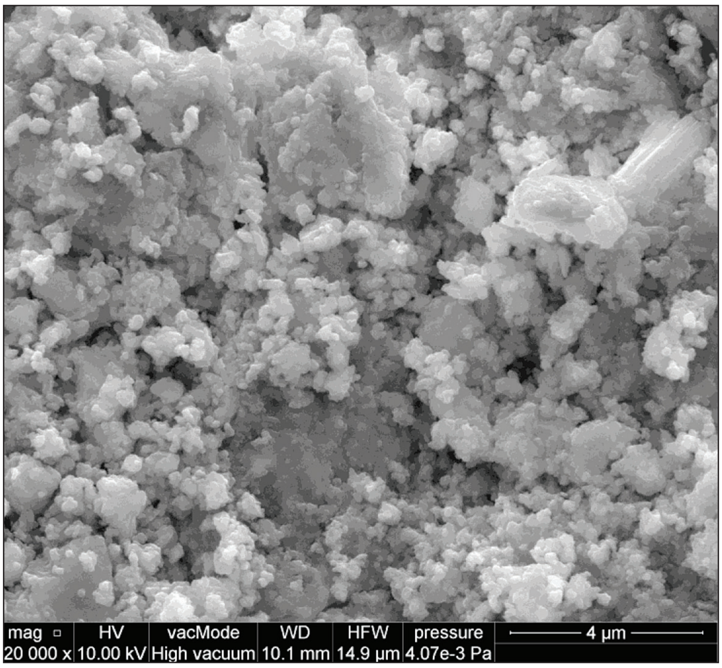

Figure 1. Microstructure of CKD (20,000×)

fineness of CKD is very small (0.10–1 µm). Portland cement primarily (> 90%) comprises particles smaller than 38 µm, while in kiln dust this fraction reaches 78%. The process of surface hydrophobization consisted in applying hydrophobizing preparations designated as follows:

- A1 – allyltriethoxysilane, $C_9H_{20}O_3Si$,
- A2 – silicone resin in toluene.

Table 3 presents the characteristics of the preparations utilized in the study.

Methods

The main characteristics of the cured samples are presented below:

- compressive strength following 28 and 56 days [39],
- flexural tensile strength following 28 and 56 days [40] (Fig. 2),
- splitting tensile strength following 28 and 56 days [41],
- specific density, total and open porosity [42],
- volumetric density [43],
- water absorption [44].

The absorption test was carried out by suspending the samples on a 10 mm mesh above the bathtub bottom; afterwards, water was poured up to half of their height. The level of water was increased after 24 h, until the samples were submerged to a depth of 10 mm. The samples were removed from water every 24 h; their surfaces were dried and subsequently weighed. Saturation of the samples was conducted until there was no further mass increase between two consecutive weighings. After saturation, the samples were dried to constant mass and weighed, followed by determining the water absorption by weight.

- absorption coefficient Cm (kg/(m^2·s$^{0.5}$)) [45]. The specimen shape was a rectangular prism having size 40×40×80 mm. The experiment was conducted under atmospheric pressure at temperature T of 23 ± 2 °C and RH = 50 ± 3%. Following drying to a constant weight, epoxy resin was used to cover the lateral sides of each specimen, to ensure 1-D water transport. One of the front sides of the specimen was

Table 3. Basic characteristics of hydrophobizing agents

Agents	Density, ρ (g/cm^3)	Surface tension, σ (N/m·10^{-3})	Viscosity, η (Pa·s·10^{-3})	σ/η
A1	0.903	22.1	2.67	8.28
A2	0.95	24.3	6.0	4.05

Figure 2. Samples during testing of the flexural tensile strength

then immersed for 24 h period in water into a depth between 5–10 mm and at the specific time intervals, the increase in specimen mass was recorded. The Cm coefficient was determined from the slope of the initial stage of the cumulative mass of water plotted vs. square root of time.

- frost resistance test [44] was determined on 150×150×150 mm test samples. The samples stayed at -20 ± 2 ºC for 240 minutes and then thawed in water for 2 hours at +20 ± 2 ºC. The compressive strength decrease and weight loss of the frozen samples were determined from the tests compared to the unfrozen reference samples. In total, 100 freeze-thaw cycles were carried out.
- secant modulus of elasticity (Ec, s) [46].
- dynamic modulus of elasticity [47, 48] (Ec, d) characterizing the samples was determined by means of the dynamic method using a C311-R frequency gauge (Fig. 3). Testing was performed at approx. 1V output voltage. The surface of samples was hydrophobized by applying the agent twice using a brush.

Studies on hydrophobization efficiency:
- absorption coefficient Cm [45] after 1, 3 days, 1 and 2 weeks.
- resistance to salt crystallization [49]. A 14% dehydrated sodium sulfate solution was used for the test, in which the samples were stored for 2 hours per cycle. The result was the percentage weight loss after 15 cycles of repeated storage in salt solution and drying at 105 ± 5 °C.
- frost resistance test [44].

In each test, six samples with dimensions in accordance with the relevant standards were accepted for testing.

Figure 3. Determination of the dynamic elastic modulus (Ec,d)

RESULTS

Physical and strength characteristics of CKD concretes

Figures 4–7 shows the physical characteristics of the tested concretes, while Figures 8–10 correspond to compressive, splitting tensile and flexural strengths. Moreover, Table 4 shows the relationship between compressive strength and tensile strength, compressive strength and modulus of rupture (flexural strength), modulus of elasticity and compressive strength of tested concretes according to [39, 40, 41, 46] and American Concrete Institute (ACI). Studies of the physical properties of concretes have shown an increase in specific and bulk density along with the amount of CKD. According to Aggarwal et al. [23], the reason may be that a more compact concrete structure forms already at the mix stage due to increased bleeding and settlement of concrete mixture. The compaction of concrete mixture resulted in a decrease in open and total porosity, weight absorption and capillary absorption. These results are consistent with the authors' study [23], in which up to 50% CKD addition as a cement replacement resulted in a reduction of 3.4–4.1% in weight absorbability. In contrast, a slow increase in water absorption was observed when the proportion of CKD was increased above 50%. The open porosity of the C30 concrete decreased by 35% compared to the reference samples. CKD addition of 5% resulted in a marginal compressive strength reduction of

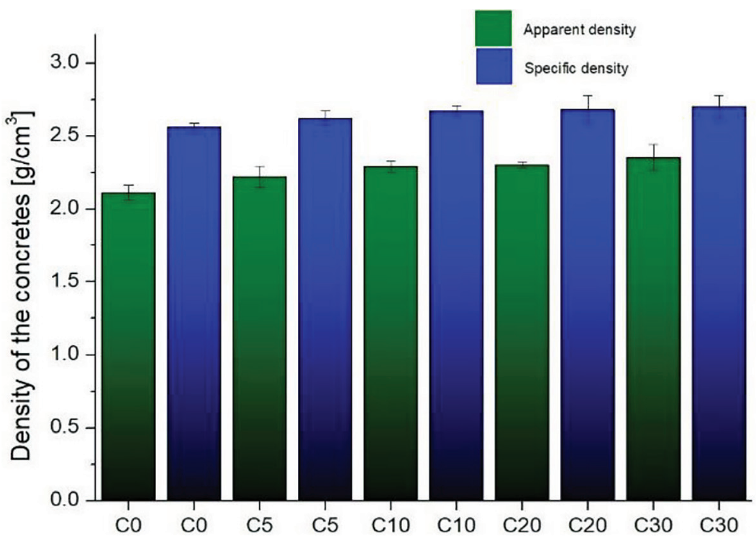

Figure 4. Density of the concretes tested

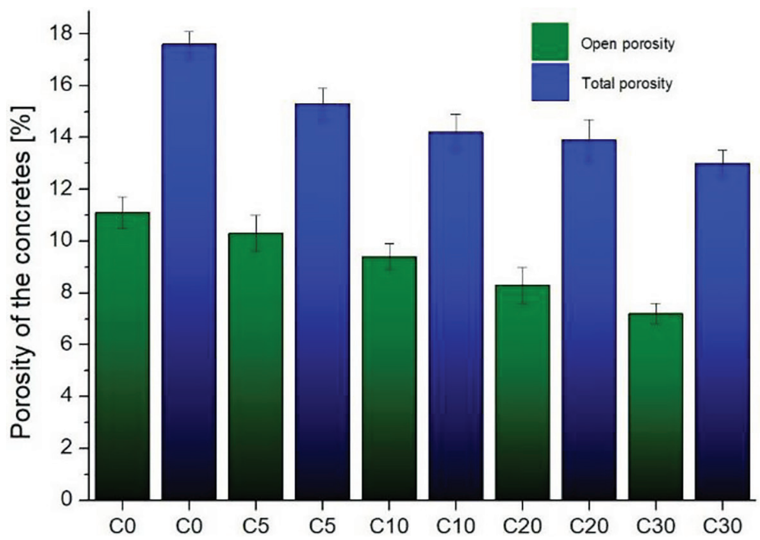

Figure 5. Porosity of the concretes tested

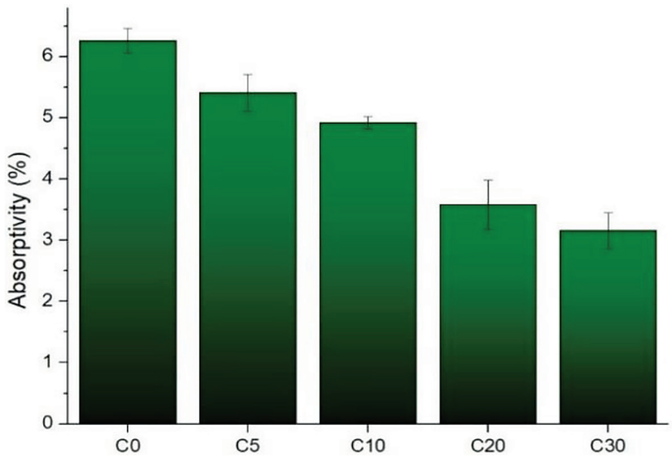

Figure 6. Absorptivity tested concretes

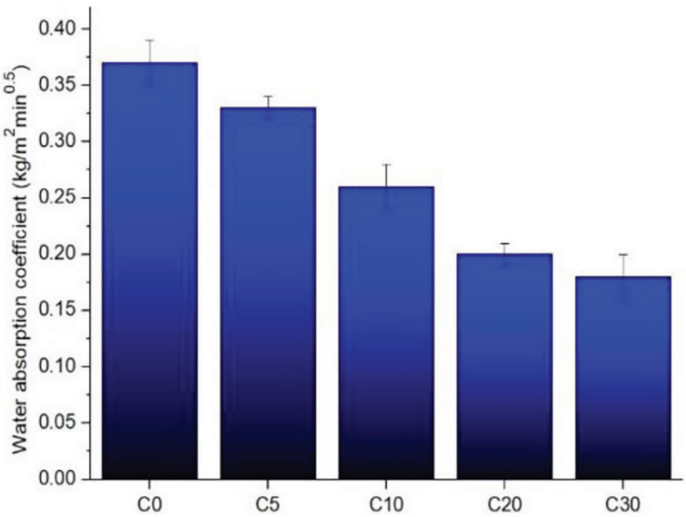

Figure 7. Water absorption coefficient of the concretes tested

Table 4. Relationship between compressive strength and tensile strength, compressive strength and modulus of rupture (flexural strength), modulus of elasticity and compressive strength of tested concretes according to [39, 40, 41, 46] and ACI

Specimen	Days	Compressive strength [MPa]	Tensile splitting strength [MPa]			Flexural strength [MPa]		Modulus of elasticity [GPa]	
			Range* according to ACI	Range** according to ACI	Value	Range*** according to ACI	Value	Value**** according to ACI	Value according to [45]
C0	28	53.4	2.9 ÷ 5.1	4.3 ÷ 7.5	5.3	5.1 ÷ 5.8	7.2	34.3	35.5
C0	56	60.3	3.1 ÷ 5.4	4.8 ÷ 8.4	6.1	5.4 ÷ 6.2	8.1	36.5	33.0
C5	28	52.5	2.9 ÷ 5.1	4.2 ÷ 7.4	5.1	5.1 ÷ 5.8	6.3	34.1	35.2
C5	56	58.8	3.1 ÷ 5.4	4.7 ÷ 8.2	5.2	5.4 ÷ 6.1	6.4	36.0	32.8
C10	28	50.0	2.8 ÷ 4.9	4.0 ÷ 7.0	5.0	4.9 ÷ 5.7	5.9	33.2	34.0
C10	56	56.2	3.0 ÷ 5.2	4.5 ÷ 7.9	5.1	5.2 ÷ 6.0	6.0	35.2	32.6
C20	28	46.1	2.7 ÷ 4.8	3.7 ÷ 6.5	4.7	4.8 ÷ 5.4	5.8	31.9	33.2
C20	56	50.1	2.8 ÷ 5.0	4.0 ÷ 7.0	4.6	5.0 ÷ 5.7	6.1	33.3	31.9
C30	28	41.1	2.6 ÷ 4.5	3.3 ÷ 5.8	4.3	4.5 ÷ 5.1	4.7	30.1	30.3
C30	56	45.5	2.7 ÷ 4.7	3.6 ÷ 6.4	4.2	4.7 ÷ 5.4	5.1	31.7	27.7

Note: *$f_{splitting}$ = 0.4 to 0.7 $(fc')^{0.5}$ [MPa], **$f_{splitting}$ = 8% to 14% (fc') [MPa], ***flexural strength = 0.7 to 0.8 $(fc')^{0.5}$ [MPa], ****modulus of elasticity E= 4700 $(fc')^{0.5}$ [MPa]

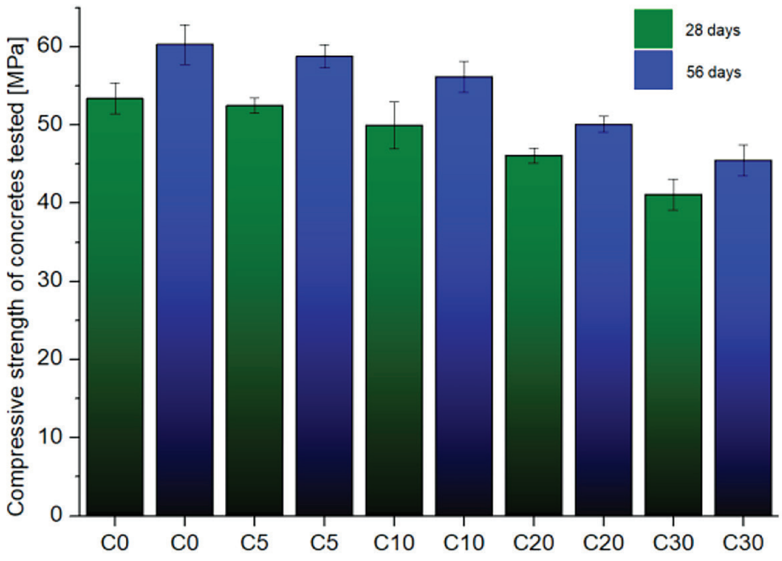

Figure 8. Compressive strength of the concretes tested

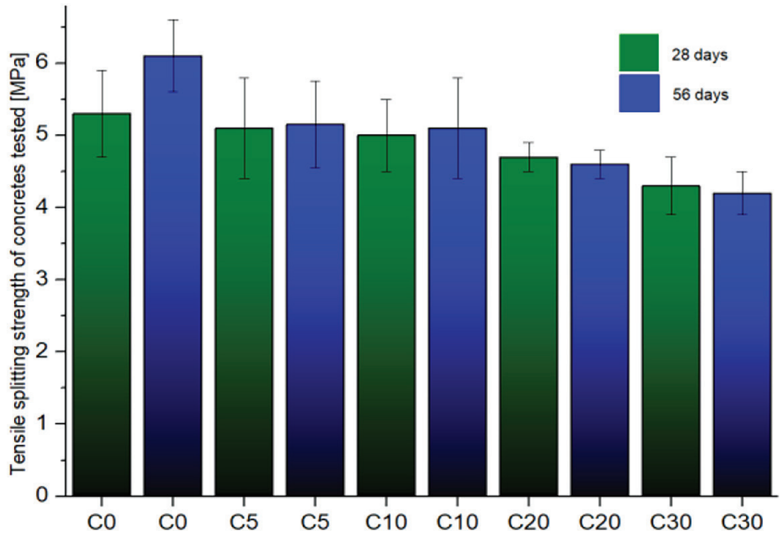

Figure 9. Tensile splitting strength of the concretes tested

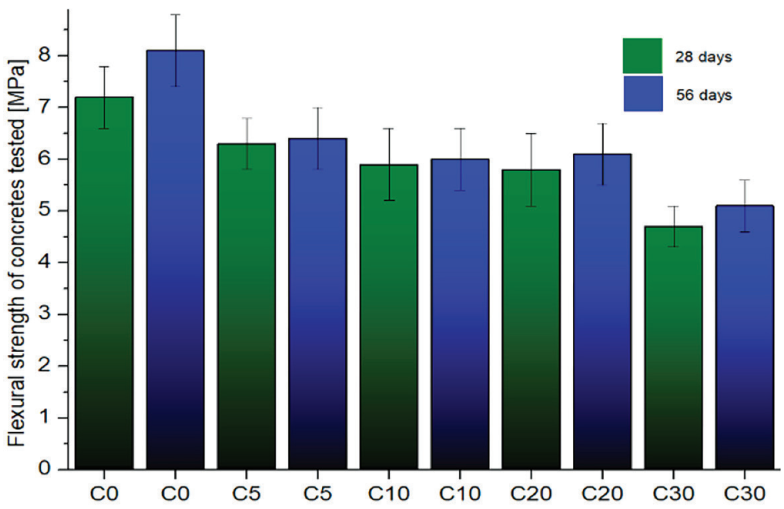

Figure 10. Flexural strength of the concretes tested

1.3% and 2.1% following 28 days (and 56 days of concrete curing. Higher admixtures of 10, 20 and 30% yielded increasing differences in strengths of 6.5% (6.9%), 13.4% (16.7%) and 23.0% (25.0%), respectively, in spite of the strength increases that occurred over time. Analogous relationships were found for flexural and tensile splitting strengths, albeit with greater differences. For instance, for the C5 concrete, the tensile splitting strength reduction is 4.5% and 16.4% following 28 days and 56 days of curing, respectively, compared to the C0 concrete. Conversely, the reduction in flexural strength is 12.4% and 21.1%, respectively. This is because neither of the tensile strengths changed in the series with dust addition, while the strength of the C0 concrete increased. It is noteworthy that in the case of the concretes with dust additive, the tensile strength values practically do not differ between 28 and 56 days of curing, regardless of the amount of additive introduced. The decreased strength of the concretes with CKD may be linked to the inert nature of CKD in comparison with portland cement. Replacing cement with CKD reduces the amount of hydration products, resulting in weaker internal structure of the concrete, and consequently lower mechanical strength. The authors [50] observed that replacing portland cement with CKD reduces the amount of calcium silicates (C_3S, C_2S) produced, which are mainly responsible for the strength of concrete. Chemical analysis of the CKDs used for the study in this article, showed a high content of K_2O (30.5%) compared to cement (0.55%). Increasing the proportion of K_2O in the binder caused a decrease in the amount of calcium silicate (C_3S) due to the reaction of the oxide with silicate, decreasing concrete strength. According to Lea [51], increasing K_2O in the binder by as little as 0.1% reduces the quantity of calcium silicate produced by as much as 3%. El-Aleem et al. [52] further stated that the decrease in mechanical strength in the concretes with CKD may be prescribed to the increased content of free calcium (CaO) in the dust, which, reacting with water, raises the volume of $Ca(OH)_2$, contributing to an increase in internal stresses that deteriorate the grout-aggregate bond and weaken the cement matrix. The high content of chlorides and sulfates in the composition of CKD contributes to the formation of chloroglinoate and sulfoglinoate phases, which contribute to the weakening and increased porosity of the cement paste [29].

Mohammad and Hilal [53] observed a relationship between the flexural and splitting tensile strengths reduction and the CKD increase (10, 30, 50)% in concretes as portland cement replacement following 7, 28 and 90 days of concrete curing. The authors cited weaker bonds between the grout and aggregate in the concretes comprising CKD addition as the cause for the reduced flexural strength.

Figure 11 shows the findings obtained from frost resistance tests conducted on the concretes. The weight loss was negligible and did not exceed 0.5% in any of the tested concretes. The decrease in strength in the C0, C5 and C10 concretes was small as well, reaching no more than 3%; however, the reduction in C20 and C30 was more significant, increasing to approximately 8–10%. Nevertheless, it is worth noting that in light of the requirements of PN-B-06250:1988 ($\Delta m \leq 5\%$, $\Delta R \leq 20\%$), the frost resistance limit criteria were met by all the tested concretes.

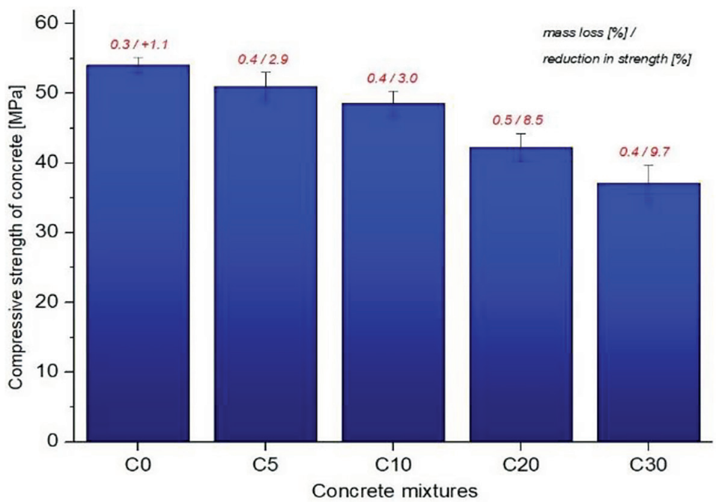

Figure 11. Compressive strength of concrete – results after the frost resistance test

Ramakishan and Balaguru [54] studied the effect of CKD as a 5% cement substitute on the frost durability of concretes after 300 freezing-thawing cycles. The concretes differed in w/c ratio, volume of cement pastes and cement type (CEM I, II and III). They found that replacing cement with 5% cement dust had no significant effect on the frost life of the concrete. Wang and Ramakrishnan [55] observed a greater decrease in the weight of the concrete specimens with 5% dust addition only after exceeding 120 F-T cycles. Up to 120 F-T cycles, no significant weight changes were observed in the concrete. The results of the secant longitudinal modulus of elasticity and dynamic modulus are shown in Figures 12–13. The structural damage of concrete due to freezing and thawing cycles is reflected in the changes of dynamic modulus of elasticity [56]. The effect of the CKD additive on the secant modulus can be considered insignificant at levels of 5 and 10% of the introduced additive. This causes 0.8 and 4.4% Ec,s reduction of the C5 and C10 concretes, respectively, compared to the modulus of the C0 concrete. When the amount of CKD additive was increased to 20 and 30%, a greater reduction in the Ec,s of the concretes was achieved, to 8.0 and 14.7%, respectively. Since concrete is an elastic-plastic material, Hook's equation can be used to describe the relationship between the secant modulus of elasticity and its strength. This equation states that stress is proportional to strain provided the material remains in the elastic limit. Thus, in the case of concrete, an indirect relationship exists between mechanical strength and Young's modulus Ec, s [57]. Usually, the higher the Young's modulus of concrete, the higher its compressive and tensile strength. Therefore, the dust addition had no significant effect on the value of Young's modulus. The concretes with higher compressive strengths obtained a higher longitudinal modulus, while the concretes containing CKD with lower strengths had a lower modulus value.

A relationship between the decrease in longitudinal modulus resulting from an increased CKD amount in concrete was also observed by Mohammand and Hilah [53]. The authors determined the static longitudinal modulus of concrete with the CKD addition at 10, 30 and 50% of the cement substitute. The study showed a decrease in modulus by 5.31, 9.67 and 77.87% in concretes containing 10, 30 and 50% CKD, respectively. The authors [53] attribute the decrease in longitudinal modulus to the lower compressive strength after decreasing the portland cement amount and the higher amount of CKD chlorides causing crystallization of hydration products and increasing the proportion of open pores in the concrete.

The F-T cycles of concretes decreased the moduli in each of the tested series. To the greatest degree in the C30 concrete – 10.4%, followed by the C0 concrete – 6.9%, C5 – 6.7%, C20 – 4.2%, and the least in the C10 concrete – 4.1%. Thus, the relationship between higher CKD additive content in concretes causing a greater reduction of elastic moduli, was absent. Such a relationship occurred in terms of weight loss and strength decrease of concretes. On the other hand, a clear relationship was noted between the differences in the moduli values of the same concretes prior to and following freezing. This confirms the influence of

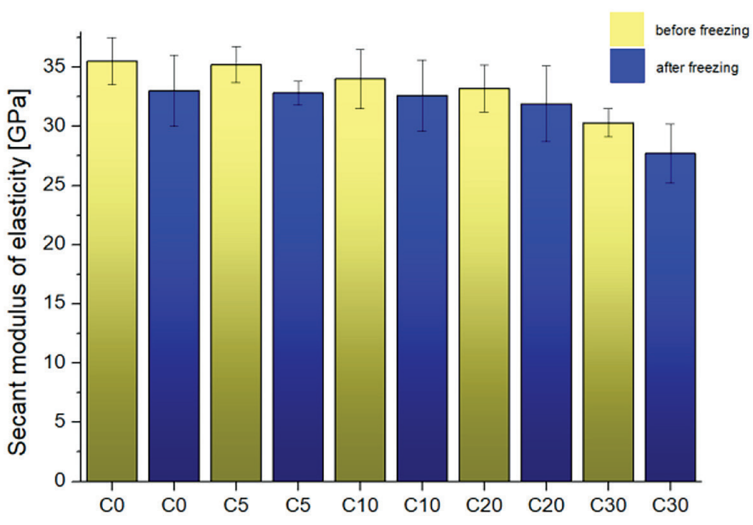

Figure 12. Results of secant modulus of elasticity of the concretes tested

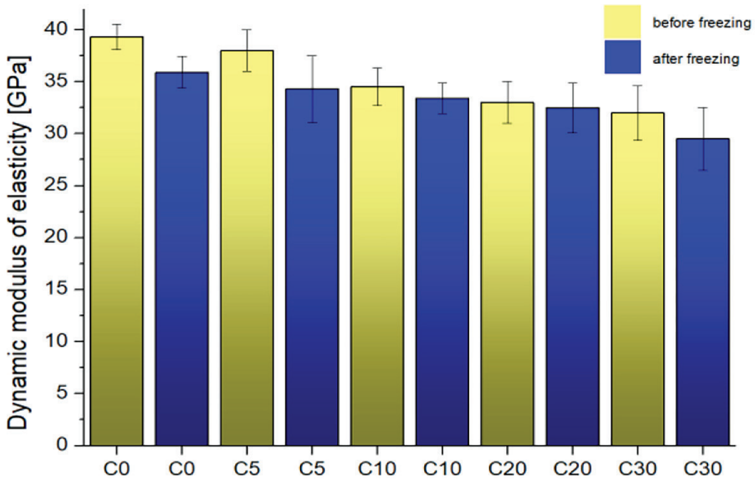

Figure 13. Results of dynamic modulus of elasticity of the concretes tested

structural changes due to freezing effect on the elastic modulus value of the concrete. As far as frost resistance is concerned, taking into account all the considered properties, the CKD addition value of up to 10% should be considered limiting.

The relative dynamic modulus of concrete comprising 5% CKD addition after 300 F-T cycles was studied by Ramakishan and Balaguru [54]. The tested concrete exhibited a decrease in dynamic modulus of no more than 10% compared to the pre-test samples. The authors found no significant differences in the modulus values for both portland cement and 5% CKD addition samples. In turn, Mohammad and Hilal [53] observed a decrease in ultrasonic wave flow velocity in the concretes with CKD addition from a value of 4.53 km/s to 4.2 k/s. The authors attributed the decrease in flow velocity connected with a dynamic elastic modulus decrease to a reduced concrete strength due to a reduction in the amount of cement and the occurrence of chlorides in the cement dust, causing greater permeability of the material.

Table 5 presented below compares the results obtained with those reported by other authors.

It is difficult to refer to the results of other authors, since they use different components, different w/b; however, the closest to the presented study is the work by Najim et al. [58]. Najim obtained compressive strength, splitting tensile strength and dynamic modulus which was higher by several percent, but with a lower w/b = 0.30. In contrast, the elastic modulus was higher by about 10–20% in the presented study. In all analyzed studies, it can be seen that as the CKD content in concrete increases, all strength characteristics decrease. No reference was found in the literature to studies of the effectiveness of hydrophobization of concretes with CKD. The findings obtained in this paper constitute new knowledge.

Hydrophobization efficiency of the concretes with CKD addition

Figure 14 shows the values of concrete absorptivity which were used in the research. The findings indicate that the hydrophobized sample has very low absorptivity, in a range of 0.2–0.94% following 1 day; however, it greatly increases following 14 days, reaching up to 4.63% in the case of the C0 reference concrete comprising methylsilicone resin. Here, the hydrophobization efficiency reached 22%, whereas for the C30 samples it amounted to 36%. The highest effectiveness was observed with a short period of contact with water. After 1 day, the hydrophobization efficiency was 59% for C0 and 84% for C30. It was found that the higher the content of CKD in concrete, the higher the hydrophobization efficiency and the lower the water absorption. This can be attributed to the dust that waterproofing the surface of the concrete.

The efficiency of impregnation of the concrete comprising CKD addition was additionally confirmed via tests of the Cm absorption coefficient (Fig. 15). This value decreases with increasing amounts of CKD in the concrete. In the C30 samples before hydrophobization, Cm value is about twice higher than in C0 concrete. following the treatment, the coefficient is one-sixth of that exhibited by the A1 formulation. The balance of increasing and inhibiting unsaturated moisture transport is primarily dependent upon the compatibility between the particle size and pore

Table 5. Physical and mechanical characteristics compared to other tests of concretes with CKD

Study	CKD replacement (%)	w/b ratio	Compressive strength (MPa)	Flexural strength (MPa)	Splitting tensile strength (MPa)	Modulus of elasticity (GPa)	Dynamic modulus of elasticity (GPa)	Absorption (%)
In this study	0	0.36	53.4	7.2	5.3	35.5	38.2	6.0
	5		52.5	6.3	5.1	35.2	37.9	5.2
	10		50.0	5.9	5.0	34.0	35.0	4.5
	20		46.1	5.8	4.7	33.2	34.5	3.4
	30		41.1	4.7	4.3	30.3	33.9	3.0
Al-Harthy et al. [34]	0	0.50	55	4.7				
	5		54	5.1				
	10		53	5.1				
	20		45	4.5				
	30		43	3.6				
Najim et al. [58]	0	0.30	65		5.4	33	44	
	10		55		4.4	30	42	
	20		52		4	27	38	
	30		47		3.5	25	35	
Sadek et al. [29]	0	0.193	62.3		4.71			2.39
	10		58.4		4.63			2.60
	20		54.2		4.16			2.95
	40		50.3		3.87			3.12

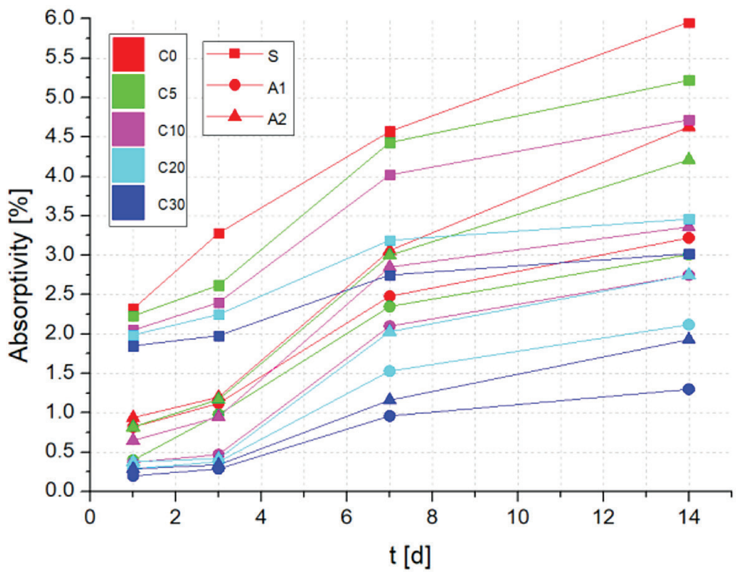

Figure 14. Absorptivity of standard and hydrophobic concrete with CKD

structure of the hydrophobic polymer within the formulation. The A1 and A2 agents used for hydrophobization, i.e. silicone resin and siloxane, differ in structure and particle size. Siloxanes are oligomeric compounds while silicone resins are polymeric compounds. The hydrophobization process occurs due to the presence of CO_2 from the air. Due to the chemical reaction, slow polymerization occurs, which leads to the hydrophobic properties of the materials through carbonation. Carbon dioxide, on the other hand, accelerates this process, while $Ca(OH)_2$ slows it down [59]. The particle size of silicone compounds influence the speed and depth of penetration of formulations into the structure of building materials. Since the particles of silicone resins are approximately 100 times larger than siloxanes, hydrophobization with the A1 formulation was found to be more effective, as evidenced by the lower absorbency and capillary absorption coefficient results. Al-Rezaiqi et al. [60] observed that the absorption of concrete

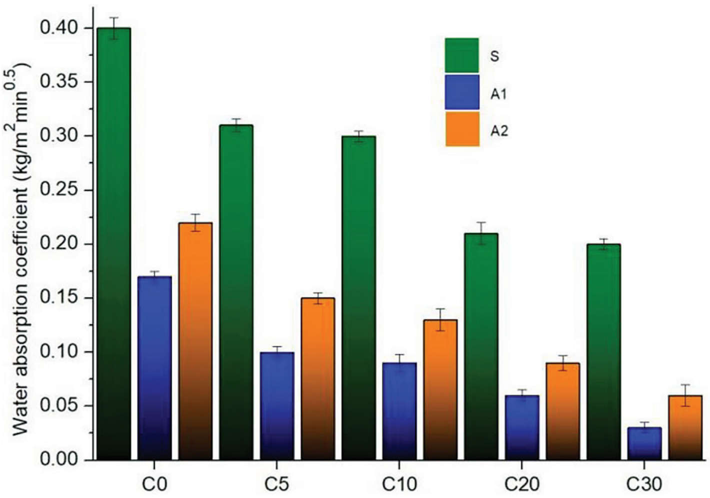

Figure 15. Water absorption coefficient of concrete with CKD

decreased as CKD increased in the amount of 20–40% portland cement substitute. In addition, it was found that with a CKD increase, the initial surface absorption of concrete also decreased.

Tests have shown higher hydrophobic properties with the A1 formulation than with the A2 formulation. This is because the methylsilicone resin, due to its large particles, does not penetrate the structure of the concrete, forming a thick gel-like sealing film on the surface of the material, which breaks during drying [61]. According to Sabatini et al. [62] an optimal hydrophobic coating should reduce the capillary rise of the material while not interfering with the diffusion process of water vapor. Earlier studies by the authors [61] showed that the adhesion between resin particles is inadequate, resulting in cracks between the largest particles. There were no such problems with the siloxane-based formulation, which did not seal the outer structure of the concrete or interfere with the diffusion of water vapor. It should be noted that too tight a surface that reduces water vapor permeability may cause damage to the cementitious material, whereas when water is present in the pores of the concrete for a prolonged period of time, it can contribute to salt crystallization.

The weight loss of all reference concretes following the frost resistance test was low, in the range of 0.2 to 0.51%, as shown in Figure 16. The influence of impregnation is clearly visible in the series with no dust addition. The treatment of the hydrophobisation reduced the weight loss of the specimens after exposure to freezing by 50%. With higher CKD content, the hydrophobization effectiveness is very low. The most favorable results were achieved for the A1 oligomers. As it can be seen from the lower absorptivity, CKD sealed the structure and surface of the concrete, which prevented sufficient penetration of the formulation into the sample. This is because the adsorption capacity of a chemical compound is governed by the pore diameter and particle size of the hydrophobic

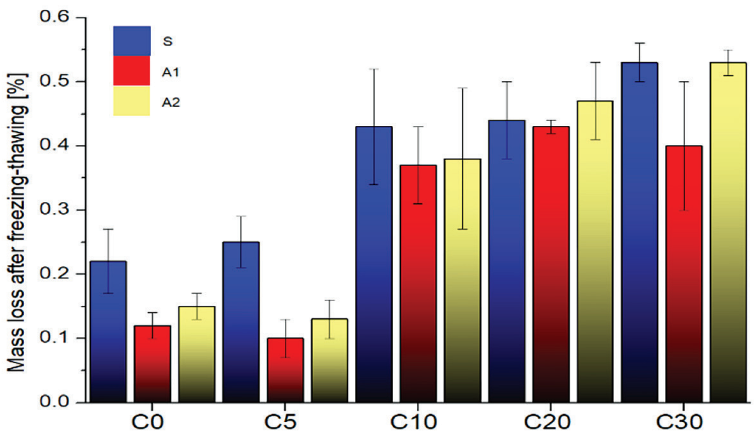

Figure 16. Weight loss of hydrophobized CKD concrete specimens after frost resistance testing

agent [63]. In addition, repeated freezing-thawing cycles caused damage to the thin hydrophobic layer, contributing to low efficiency of the process.

Sulfate corrosion of concrete belongs to a group of chemical corrosion caused by the presence of sulfate anions SO_4^{2-} most often originating from ground, sea or underground water, which, penetrating into concrete, react with hydrated calcium aluminates to form expansive ettringite leading to cracks in the material. The most common method of protection against sulfate corrosion is the use of high sulfate-resistant (HSR) cements [64].

In this paper, the resistance against salt crystallization in the microstructure characterizing CKD concretes was determined as the weight loss/increase of the specimens following 15 cycles of storage in 14% $Na_2SO_4 \cdot 10H_2O$ solution and drying at 105 ± 5 °C. The obtained results are shown in Figure 17. The tested samples were preserved in very good condition. The material surface was not damaged in a visible way. Following 15 test cycles, the samples with having CKD content indicated weight loss. This is due to the lowest porosity and absorption of these samples, resulting from the sealing capability of the abundant presence of CKD. During crystallization, sulfate salts increase their volume 10 times. With the reduced amount of concrete free pores, as well as the decreased compressive strength, the hydrophobic sample and reference sample (C30) both experienced slight damage in the range of 0.08 to 0.1%. The weight of the samples experienced an increase (by as much as 0.09%) in majority of cases, due to internal salt crystallization. The weight gain of the samples was reduced via hydrophobization due to the surface sealing of the material [65, 66].

Al-Harthy et al. [34] observed that the inclusion of a small CKD addition to cement mortar reduced the sorptive properties of the material resulting in improved absorbability, decreased permeability and improved mortar durability. Reduced permeability of concrete provides higher resistance to sulfate absorption and higher protection against chemical corrosion. When analyzing the available literature, there is a correlation between the increase in permeability along with the amount of CKD in concrete. In turn, El-Sayed et al. [33] found that in cement mortars, the CKD addition up to 5% protects against chemical corrosion due to the presence of aggressive chlorides and sulfates in the mixture. Batis et al. [67] studied the corrosion resistance of reinforcement concrete steel with 6% CKD of two different chemical compositions. They observed that the chemical composition of CKD affects the corrosion of steel in concrete. While the concretes with CKD with lower chloride and sulfate ion content show higher chemical corrosion resistance, the concretes with CKD with higher aggressive ion content and lower alkalinity have lower corrosion resistance regardless of the water-cement ratio. According to [68] the permeability of concrete can be reduced by increasing the specific surface area of CKD particles, which, behaving like fine dust, can seal the concrete structure.

In our article, no chemical, microstructural studies were carried out, however we can refer to the studies of other authors, e.g. [66]. They observed during SEM tests that surface hydrophobization with nano-silanes has a slight impact on cement hydration process, although cement hydration products are in all cases characteristic for III and IV morphological types of C-S-H phases.

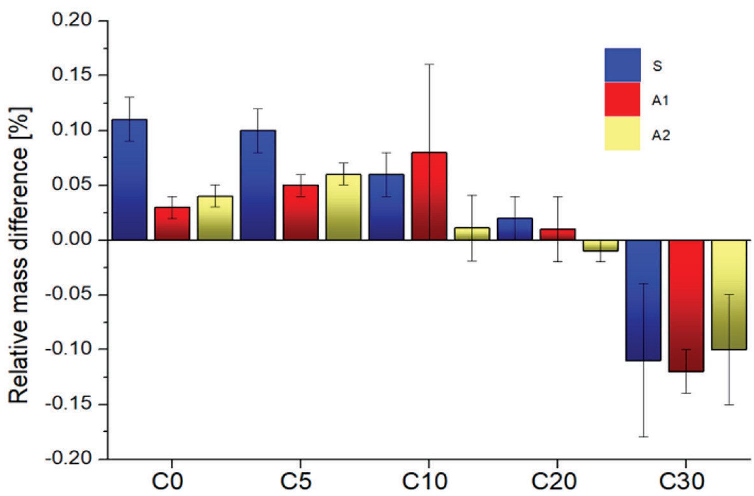

Figure 17. Differentiation in mass after salt crystallization process

However, with the hydrophobisation of nanopolymer, the surface morphology becomes denser and the pores are filled with a newly created skeleton. According to Palou et al. [69] in the earlier period of hydrothermal hardening, hydrated C-S-H products were formed during the chemical process. Partial thermal decomposition of the mortars takes place under high pressure at a later stage of the curing process, which results in saturation of the sample with carbon dioxide [69]. Additionally, the silane content on the sample surface slows down the cement hydration, influencing the quality and type of produced phases. There are no visibly crystallized ettringite particles in mortars. Figures SEM show a shallow rather than spherical structure of the phases, as opposed to a typical cement mortar. This indicates that the silane content caused changes in the mortar structure. This is reflected in the results of physical characteristics tests, where it was shown that the coating seals the surface of the samples. The size of silicone gel particles ranges from 0.5 µm to 5 µm. Nanosilane gel particles are closely packed, closely adhere to each other, form a compact film without cracks, which contributes to higher hydrophobic properties and lower absorption. In the case of the siloxane formulation, the gel particles are dispersed, vary in diameter, and do not thoroughly cover all the components of the mortar. This results in lower hydrophobization efficiency, higher water absorption, and a decrease in frost resistance and salt resistance, as confirmed by earlier studies by Szafraniec et al. [66], as well as hydrophobized lightweight mortars described in the literature [59, 63]. The correlations between the value of the dynamic modulus and the compressive strength of concrete are shown in Figure 18. Studies showed a correlation between the compressive strength and dynamic modulus of concrete of 0.808. The dynamic modulus was observed to increase along with the compressive strength of concrete; the strongest correlation was found in C0 and C5 specimens. Jurowski and Grzeszczyk published a paper describing the relationship between dynamic modulus and compressive strength [70]. The authors reported that in order to establish a relationship between these two parameters, it is necessary to first determine a relationship between the dynamic modulus of elasticity and the initial static modulus of concrete. The relationship proposed by the authors accounts for the type and quantity of aggregate as well as the type of the employed binder. The study showed that taking these factors into account allows a more accurate calculation of compressive strength. The authors' results showed that the stabilized modulus of elasticity depends on the initial modulus of elasticity, with the coefficient of proportionality between the two depending on the type of aggregate. Zhou et al. [71] observed a relationship between the dynamic and static moduli of elasticity as well as the volumetric content and maximum dimension of aggregate grains. The correlation between dynamic and static moduli can also be found in [71, 72, 73]. According to Lee et al. [74], the shape of the sample is of great importance, Salman and Al-Amawee [75] state that the modulus of elasticity depends on the type and composition, while Plachy et al. [72] believe that determining the appropriate test methodology is influential. Shkolnik, on the other hand, proposed a relationship between the dynamic and static moduli as well as the level of applied stress in a static test and the rate of applied load [73].

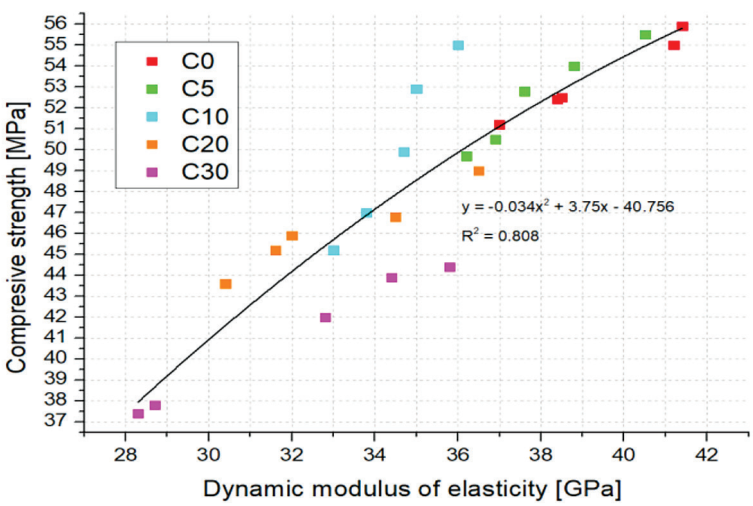

Figure 18. Correlation between compressive strength and dynamic modulus of elasticity for all testedconcretes

CONCLUSIONS

The influence of surface hydrophobization of concrete with CKD was investigated in the study. The following key conclusions were drawn: Physical and mechanical characteristics of concretes with CKD:

- Research on the physical properties of concretes showed an increase (up to 10%) in specific and bulk density along with the CKD amount.
- As the CKD content increases, the porosity of the concrete decreases. The open porosity of C30 concrete decreased by 35% compared to the reference concrete.
- The 5% dust addition slightly decreased compressive strength by 1.3% and 2.1 following 28 and 56 days of concrete curing, accordingly. When the CKD amount was increased over 10%, greater strengths differences were achieved, amounting to 6.5% (6.9%), 13.4% (16.7%) and 23.0% (25.0%), respectively, in spite of the strength increase that occurred over time. Similar relationships were found for flexural and tensile splitting strengths. Regarding to C5 series, the tensile splitting strength reduction is 4.5% and 16.4% following 28 days and 56 days of curing, respectively, compared to the C0 concrete. Conversely, the flexural strength reduction is 12.4% and 21.1%, respectively. Reduced strength of the concretes with CKD can be attributed to the inert nature of CKD compared to portland cement. Replacing cement with CKD reduces the amount of hydration products, resulting in a weaker internal structure of the concrete, and thus lower mechanical strength.
- The effect of the CKD additive on the secant modulus can be considered insignificant at levels of 5 and 10% of the introduced additive. This reduces the Ec, s by 0.8 and 4.4% for the C5 and C10 concretes, respectively, compared to the modulus of the C0 concrete. When the amount of CKD additive was increased to 20 and 30%, the Ec, s reduction of concretes was more significant, reaching 8.0 and 14.7%, respectively.
- The study showed a correlation between the compressive strength as well as dynamic modulus of concrete equal to 0.808. Findings indicate that the dynamic modulus of the concrete increased along with its compressive strength.
- Throughout the frost resistance testing of all concrete specimens, negligible weight loss occurred, totaling less than 0.5%. The strength reduction in the first three series of concrete was small as well, less than 3%; however, in the C20 and C30 concretes the reduction was more significant, increasing to approximately 8–10%.
- In line with the conclusions drawn from authors' previous investigations, CKD utilization is highly prospective; nevertheless, it should be remembered that the 5% share limit shares in the composition of concrete is viable and has no negative impact on the concrete parameters. Its share is acceptable up to 10%, but the 20% admixture should not be exceeded because all final product parameters experience reduction. In terms of the durability of concretes to frost effects, taking into account the calculated properties, the 10% limit value of dust admixture should not be exceeded.

Water-repellent effectiveness of the concretes:

- The hydrophobized samples exhibit very low absorptivity, in the range of 0.2–0.94% following 1 day; however, it significantly increases following 14 days, reaching up to 4.63% in the case of the C0 reference concrete with methylsilicone resin (A2). For the reference sample, the efficiency hydrophobization equaled 22%, while the C30 achieved 36%. The highest effectiveness was attained when contact time with liquid was inconsiderable. Following 24 hours, the effectiveness of impregnation was equal to 59% for C0 and 84% in the case of C30. The greater the cement kiln dust content in samples, the higher the hydrophobization efficiency and the lower the water absorption. This occurs because the dust seals the surface of the material.
- The water-repellent effectiveness in the case of the samples with kiln dust was also proven via the research on the coefficient Cm. The higher the kiln dust content in material, the closer the Cm value gets to zero. (Tab. 7).
- All of the reference concretes had low weight loss in the range of 0.2 to 0.51% after the frost resistance test. The most noticeable hydrophobization effect is observed in the concrete lacking CKD. The most favorable outcomes were achieved for the A1 oligomers. The lower absorptivity indicated that CKD sealed the structure and surface of the concrete, which prevented the formulation from sufficiently penetrating into the sample. This is because the adsorption capacity of a chemical compound is governed by the particle size and pore diameter of the hydrophobic agent.

- As a result of the reduced quantity of free pores in the concrete with CKD, in addition to the lower compressive strength, the reference sample (C30) as well as the hydrophobic sample both experienced slight damage in the range of 0.08 to 0.1% after the crystallization test of sulfate salts. The sample weight in majority of cases increased (by up to 0.09%) due to the internal crystallization of the salts.

To conclude, the use of cement dust reduces cement consumption, which translates into lower carbon dioxide emissions into the atmosphere. The cement production process is one of the main sources of CO_2 emissions, so any alternative used that reduces cement consumption contributes to decreasing greenhouse gas emissions. Cement dust comes from industrial waste products, such as fly ash from coal-fired power plants or waste from cement production. Using the waste for concrete manufacturing is a form of recycling and helps avoid landfilling. The use of CKD in cement production is beneficial from both economic and environmental perspectives. It can help reduce the cost of cement production and reduce the negative impact of cement production on the environment. However, it is necessary to monitor and control the process of using CKD in cement production to ensure optimal economic and environmental conditions. Limitations of cement dust applications may include its availability, price, technological difficulties associated with its use, or concrete quality problems. Further research should include improving the technology for producing concrete with CKD, combining cement dust with other additives to improve concrete properties, researching alternative mineral raw materials to replace cement, and developing methods for monitoring the quality of concrete with cement dust. In addition, as it was already mentioned in the manuscript, the composition of dust and the properties of the material with CKD vary from one cement plant to another, it becomes fully justified to continue research on the properties of building materials with this material. An economic analysis of the use of dust in cement production shows that it can be a cost-effective solution for both cement producers and the environment. The use of CKD as an additive in cement reduces production costs by decreasing the consumption of natural resources and energy required for cement production. In addition, the reduction in landfill waste translates into reduced costs for disposal and reclamation of landfill sites. The use of CKD in cement production is beneficial from both economic and environmental perspectives. It can help reduce the cost of cement production and reduce the negative impact of cement production on the environment. However, it is necessary to monitor and control the process of using CKD dust in cement production to ensure optimal economic and environmental conditions. It can help reduce the cost of cement production and mitigate the negative impact of cement production on the environment. However, it is necessary to monitor and control the process of using CKD in cement production to ensure optimal economic and environmental conditions.

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