

Article

# Zeolite Tuff and Recycled Ceramic Sanitary Ware Aggregate in Production of Concrete

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**Abstract:** The article presents the results of research on the use of ceramic ware waste as aggregate in concrete production. Four concrete mixtures with aluminous cement were prepared, each with a different admixture of clinoptilolite. The only used aggregate was crushed waste ceramic sanitary ware obtained from a Polish sanitary fixture production plant. As part of the studies, a compressive test of cubic samples at different curing times ranging from 7 to 90 days was performed. Prior to the preparation of the samples, a sieve analysis and an elemental analysis of the obtained aggregate were conducted. In the framework of the testing, the bimodal distribution of clinoptilolite grains was determined, as well as its chemical composition. The conducted compressive tests demonstrated high strength of concrete containing ceramic aggregate and aluminous cement with an addition of clinoptilolite. In order to determine the impact that adding zeolite exerts on the phase composition and the structure of concrete samples, an analysis of the phase composition (XRD) and scanning electron microscopy examination (SEM) were performed. Furthermore, tests of abrasion, water penetration under pressure and frost resistance were conducted, determining particular properties of the designed mixtures. The abrasion tests have confirmed that the mixtures are highly abrasion-resistant and can be used as a topcoat concrete layer. The conducted tests of selected properties have confirmed the possibility of using waste ceramic cullet and a mineral addition of clinoptilolite in concrete production.

**Keywords:** zeolitic tuff; recycled aggregate; ceramic sanitary ware; concrete

## 1. Introduction

Over the 20th and 21st centuries, a growing demand for ecological, economical, durable and flexible construction materials has become quite a serious challenge for process engineers specialising in cement and concrete. Recently, the introduction of mineral additives to cement and concrete has turned out to be a valuable solution. They play an important role in shaping the properties of construction binders, as well as of the concrete mixture and concrete [1]. Mineral additives—both pozzolan and hydraulic ones—modify the phase composition of cement paste in order to reduce portlandite and to change the ratio of CaO/SiO<sub>2</sub> in phase C–S–H [2], above all.

One of the directions of ongoing subject studies is concerned with the application of zeolitic tuff as a pozzolanic additive to concrete. Zeolites constitute a group of hydrated tectoaluminosilicate characterised by catalytic, adsorptive and ion exchange properties. Given their specific structure, zeolites are a natural material that is ecologically pure, neutral and nontoxic, appropriate for various uses in industry, agriculture, households and construction [3,4]. Zeolites are regarded as an important component of concrete, as well as in the development of concrete and new construction materials, such as high-strength concrete, concrete characterised by the absorption of heavy metals or metals protecting

against radiation. The addition of zeolites accelerates the hydration process and simultaneously enables the production of slenderer structural elements without impairing their properties related to strength [5].

As part of the study [6], strength tests of concrete with the additive of 5% to 40% of zeolitic tuff in the cement mass were conducted in diverse periods. It was found that in the compressive tests, conducted after 1, 2 and 7 days, the addition of zeolite led to reduced strength as compared to control samples. In turn, for samples after a 28-day curing period, a significant increase in strength was recorded, as high as 22.3%, for samples containing 20% of zeolite. In the studies [7], cement was supplemented with 5–35% of zeolite. In this particular case, also compressive strength at different time intervals, including after 90 days, was examined. It was proven that the addition of 20% of zeolite improves the compressive strength of concrete samples after a 28-day curing period. Moreover, studies carried out by [8,9], where concrete mixtures containing zeolite were designed, confirmed that at an early curing stage, the compressive strength of concrete with the addition of zeolite is lower than in the case of reference concrete. Similarly, attempts to use zeolites as additives in high-strength, self-compacting concrete [10] were made. In the studies in question, four mixtures with the addition of 10 and 15% of zeolite or pumice were produced, as well as a control mixture without any additives. Compressive testing was carried out at different curing times (3–365 days). In the conducted tests, zeolite was found to have a higher pozzolanic activity as compared to pumice.

High-strength, self-compacting concretes containing zeolite show high porosity and low compressive strength, compared to control concretes. This is due to rheology problems related to the compatibility of the studied zeolite with some concrete components and with the used superplasticizer in particular. The substitution of 10% of ordinary Portland cement with pumice increases compressive strength in both early and late maturing periods.

Furthermore, the tests showed that concrete with the addition of zeolite is characterised by limited penetration of chloride ions, as well as enhanced resistance to penetration of water. Tests of the impact exerted by high temperatures on concrete containing the additive of clinoptilolite are also being carried out.

In the study [11], six concrete mixtures comprising 5–40% of clinoptilolite were designed. Compressive testing of thermal conductivity was conducted, as well as of the impact of high temperatures within the range of 250–1000 °C. The temperature in the furnace increased by 8 °C/min, and samples were kept there for 2 hrs. The samples subjected to thermal processing were cooled down using two methods (slow cooling and rapid cooling). The results of the tests showed that the additive of clinoptilolite reduced the compressive strength of samples in an early stage of concrete hardening, simultaneously increasing it after 28 days. The conducted microscope analysis showed that with an increase in the amount of added clinoptilolite, the susceptibility of concrete mixtures to high temperatures was lower. Furthermore, the method of rapid cooling caused a more significant reduction in compressive strength as compared to the slower cooling of samples. It may result from higher thermal gradients during rapid cooling, regardless of the type of concrete. In addition, the application of clinoptilolite reduced the value of the coefficient of the thermal conductivity of concrete.

Approximately 70–80% of the concrete volume is constituted by aggregate [12]. Current trends in industrial concrete production and the legislation of the European Union recommend the use of recycled aggregate (RA) [13]. Research to date shows that recycled aggregate of many beneficial parameters is obtained from crushed whiteware ceramics. The papers [14–16] describe the basic parameters of this type of aggregate. It has been proven that, as regards fracture strength, recycled whiteware aggregate may be categorised as LA<sub>25</sub>, which, in terms of natural aggregate (NA), corresponds to granite, gravel or quartzite aggregate. The obtained results with respect to bulk density (2403 kg/m<sup>3</sup>) and the average absorbability of 1.98% mean that the density of ceramic aggregate is similar to the density of such natural rocks as granite or marble, and the absorbability is similar to that of dolomite or gravel with the prevalence of carbonate particles. Furthermore, during the testing of

frost resistance, the weight loss equalled 0.29% (i.e., the aggregate achieved the highest frost resistance category F<sub>1</sub>).

Tests of concrete containing ceramic whiteware aggregate have confirmed that the concrete is characterised by a relatively high strength and resistance to an aggressive environment, and has several other advantageous properties discussed below. This was in turn confirmed by the studies [17–19] in which only recycled aggregate of ceramic whiteware was used. A positive impact of the use of recycled ceramic aggregates (RCA) consisting of ceramic whiteware was also confirmed in the tests of [20], in which 20 and 25% of coarse NA were replaced with recycled aggregate consisting of crushed ceramic whiteware. It was proven that electrical resistance grows with the use of recovered aggregate owing to the inherent properties of this material. Furthermore, the designed concrete types were found to have considerable strength and durability as compared to natural aggregate concrete.

Given the high temperature of baked whiteware, attempts are also being made at using crushed ceramics as aggregate for special types of concrete resistant to high temperatures.

In the framework of the studies [21,22], tests of the material properties of concrete containing aluminous and Portland cement, and concrete containing only ceramic ware aggregate were carried out. Samples were subjected to thermal loads at the temperature of 1000 °C. It was found that parts of the samples were subjected to an explosive spalling during the heat treatment. This was the case for the samples that contained aluminous cement, in particular. That phenomenon was successfully limited by the application of an aerating admixture enabling 10%-degree aeration of the concrete mix. At the same time, the application of the additive resulted in enhancing the residual strength after the heating process. Nevertheless, the tests [23] showed that concrete with ceramic aggregate is characterised by high heat accumulation after the heating process. In the authors' opinion, this type of concrete can be used as cladding of storage heaters, among others. Undoubtedly, the use of recycled aggregate and pozzolan additives is environmentally friendly, which is currently of considerable importance owing to the growing ecological awareness of both communities and concrete producers.

The research is a continuation of the authors' tests of concrete samples containing recycled ceramic aggregate [15,17,21]. The material characteristics of the samples were additionally determined after subjecting them to the influence of high temperatures and humidity. The use of a zeolite additive in such types of concrete is a novelty.

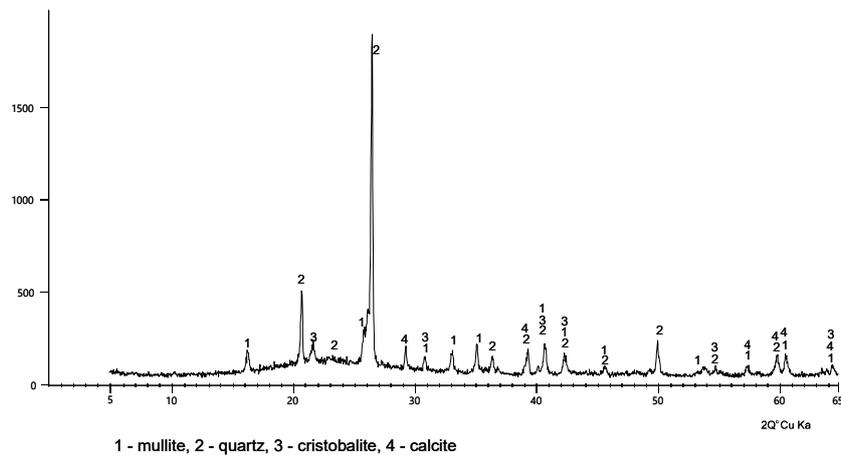
## 2. Concrete Components and Experimental Tests

The research concerned a concrete mix containing the following components: ceramic aggregate, aluminous cement and zeolite, and aimed at determining the chemical and mineral composition, as well as general characteristics of the materials used. The determination of the mineral composition of the particular components contained by the designed concrete mixes was carried out with the use of X-ray diffraction (XRD). In addition, the ceramic aggregate was subjected to testing by means of SEM-EDS to find its chemical composition.

### 2.1. Ceramic Aggregate

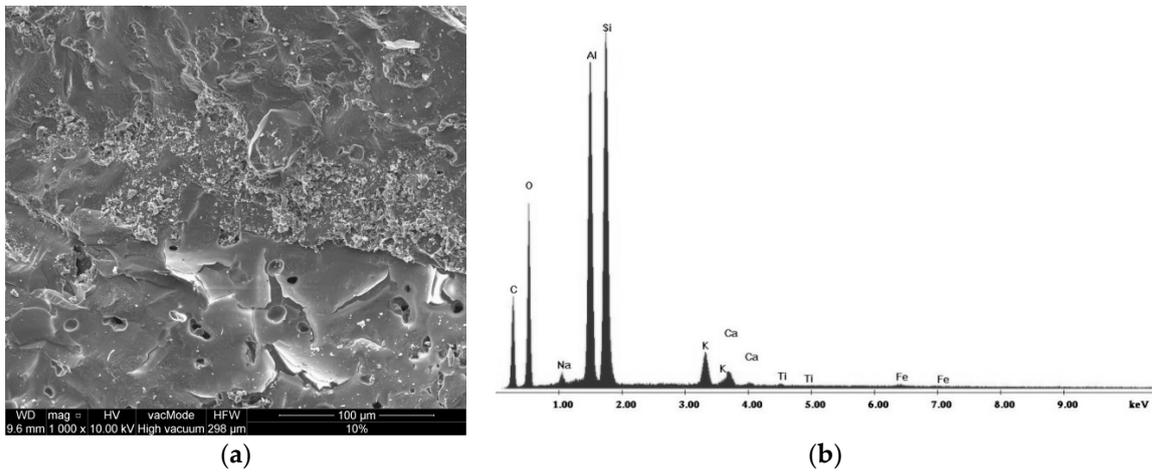
In the tests, waste ceramic whiteware obtained from used products, manufactured by a Polish sanitary fixtures production plant, was used.

The diffraction pattern of the phase composition of the aggregate is presented in Figure 1. The main mineral component of the ceramic aggregate was mullite, determined by the characteristic interplanar distances  $d_{hkl} = 5.376; 3.425; 3.390; 2.882; 2.427; 2.294; 2.208 \text{ \AA}$ . There was also quartz, determined from  $d_{hkl} = 4.255; 3.344, 2.456; 2.283; 2.237; 2.128 1.981 \text{ \AA}$ , cristobalite  $d_{hkl} = 4.055; 3.140; 2847; 2486 \text{ \AA}$ , and calcite  $d_{hkl} = 3.861; 3.040; 2283; 2096 \text{ \AA}$ . Apart from the crystalline phases, the tested aggregate comprised an amorphous substance (aluminosilicate glaze), made visible in the diffraction patterns through rising of their background within the angle range from 15 to 35 (2 $\theta$ ).

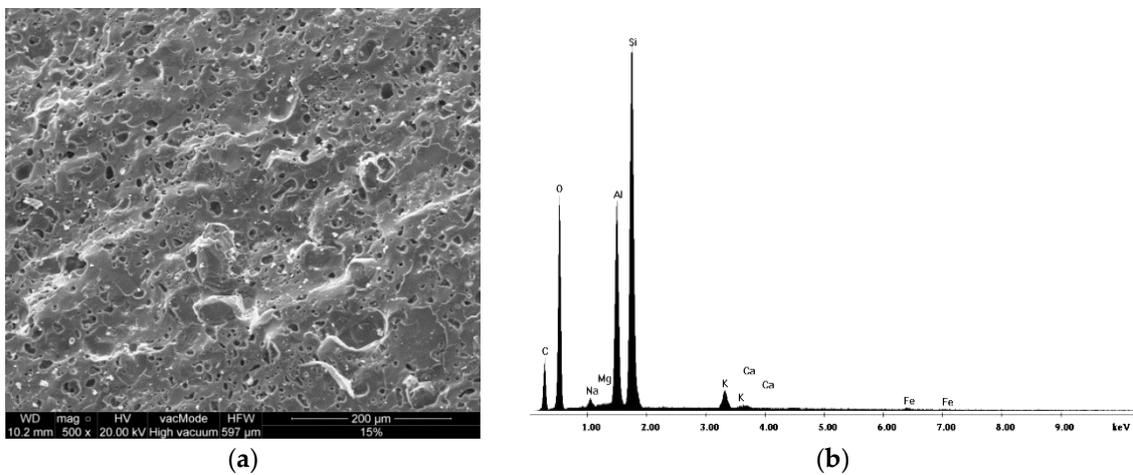


**Figure 1.** Diffraction pattern of the mineral ingredients of the ceramic aggregate.

Figure 2; Figure 3 present SEM imaging of the ceramic aggregate structure. The obtained results are presented in Table 1.



**Figure 2.** (a) View of the ceramic aggregate microstructure, 1000× enlargement. (b) EDS elemental analysis of the area visible in the image.



**Figure 3.** (a) View of the ceramic aggregate microstructure, 500× enlargement. (b) EDS elemental analysis of the area visible in the image.

**Table 1.** Chemical composition of the ceramic aggregate used in the prepared concrete mix.

Determination	Contents of Compounds [%]							
	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	K <sub>2</sub> O	CaO	Fe <sub>2</sub> O <sub>3</sub>
Analysis of area (Figure 2)	1.16	-	41.82	50.63	0.95	3.26	1.85	0.95
Analysis of area (Figure 3)	1.03	0.17	33.14	62.27	-	2.24	0.45	0.71

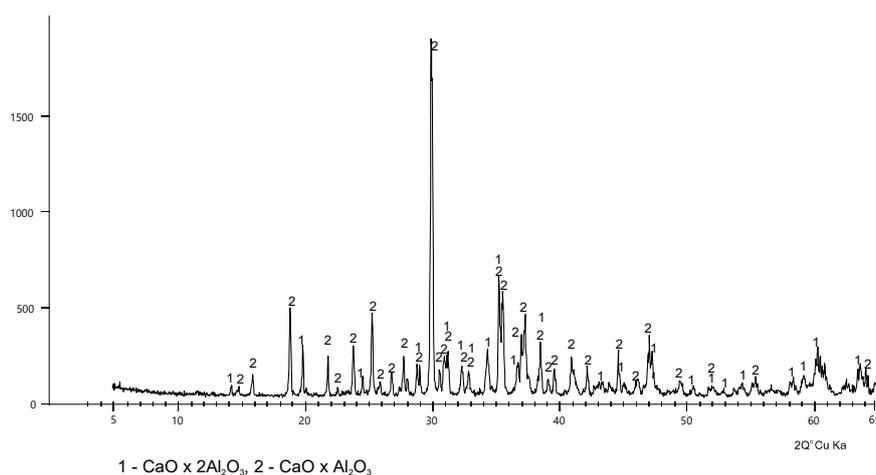
The presented photographs and analyses (Figures 2 and 3) suggest that the structure of the aggregate is similar, and their common feature are the pores recorded in the material volume. The photographs show that pore walls have a varying structure, their distribution in the material is not uniform and their intensity varies as well. The conducted elemental analysis of the ceramic aggregate showed that it contains primarily silica SiO<sub>2</sub> (50.63–62.27%) and aluminium dioxide Al<sub>2</sub>O<sub>3</sub> (33.14–41.82%), as well as potassium oxide K<sub>2</sub>O (2.24–3.26%) and sodium oxide Na<sub>2</sub>O (1.03–1.16%), and also trace amounts of iron trioxide Fe<sub>2</sub>O<sub>3</sub>, magnesium oxide MgO, and titanium oxide TiO<sub>2</sub>.

During the conducted tests, the crushing resistance of the aggregate was determined pursuant to [24]. The aggregate with the grading of 4–8 mm was tested. The average crushing index equalled 6.75%, which suggests that waste ceramic whiteware aggregate is resistant to crushing [25].

## 2.2. Aluminous Cement

In the tests, aluminous cement Górkal 70, manufactured by Górkal Cement Sp. z o.o., was used. The main binding agent of the cement is Al<sub>2</sub>O<sub>3</sub>. The chemical composition of the aluminous cement is dominated by: Al<sub>2</sub>O<sub>3</sub>—69–71%, CaO—28–30%, SiO<sub>2</sub> < 0.5%. The remaining ingredients are as follows: Fe<sub>2</sub>O<sub>3</sub> < 0.3% and Na<sub>2</sub>O < 0.3%. Selected physical parameters of the aluminous cement were: a specific surface area of 4000 ÷ 5000 cm<sup>2</sup>/g, the commencement of setting >300 min, the end of setting <600 min, the compressive strength after 24 h ≥30 MPa. The testing of the aluminous cement was carried out in conformity with the Polish standards PN-EN 196-6:2011 [26], PN-EN 196-3:2016 [27], PN-EN 196-1:2016 [28].

The mineral composition of the obtained binder is presented in Figure 4.

**Figure 4.** Diffractogram of the mineral composition of aluminous cement Górkal 70.

The dominating crystalline phase that occurs in the aluminous cement is calcium monoaluminate (CA), accompanied by calcium bialuminate (CA<sub>2</sub>). The former was determined by the characteristic interplanar distances  $d_{hkl} = 5.956; 5.529; 4.687; 4.052; 3.718; 3.309; 3.199; 2.974; 2.911$  Å, and the latter by  $d_{hkl} = 6.185; 4.448; 3.506; 2.850; 2.601$  Å. In the case of Portland cement, the main components comprise alite C<sub>3</sub>S and belite C<sub>2</sub>S, which are the main ingredients of clinker, and tricalcium aluminate C<sub>3</sub>A, as well as brownmillerite C<sub>4</sub>AF (tetra-calcium aluminoferrite).

### 2.3. Additive Used in Designed Concrete Mixtures

In the study, a natural mineral, zeolite clinoptilolite, derived from rock (zeolite tuff), quarried in the Sokyrnytsya mine (the Transcarpathian region, Ukraine) was used. The quantitative content of zeolite tuff in the sample amounted to approx. 75%. The properties of natural zeolite are: density 2135 kg/m<sup>3</sup>, specific surface area 18.33 m<sup>2</sup>/g, porosity 54.76%, total pore surface area 11.15 m<sup>3</sup>/g, average pore diameter 0.210 μm, absorbability 50% [29,30]. The other ingredients of natural zeolite are opal CT, quartz and feldspar [29]. The chemical composition of the zeolite is: 73.9% SiO<sub>2</sub>, 13.6% Al<sub>2</sub>O<sub>3</sub>, 2.79% Fe<sub>2</sub>O<sub>3</sub>, 0.63% Na<sub>2</sub>O, 4.02% K<sub>2</sub>O, 0.297% MgO, 3.75% CaO and minor amounts of other ingredients, such as MnO, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Cl [28]. Figure 5 presents a microphotograph of particle clusters in clinoptilolite.

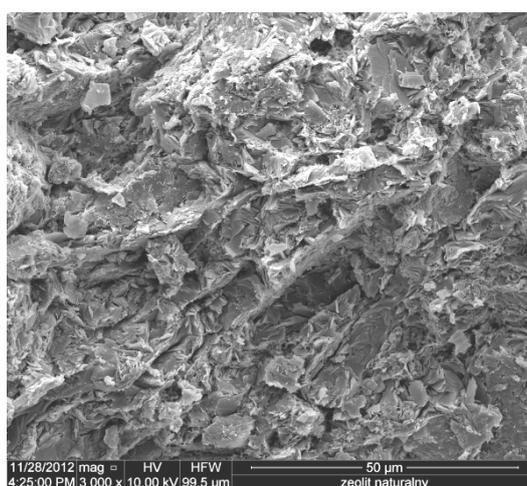


Figure 5. Microphotograph of clinoptilolite grain clusters; 3000× enlargement.

The dominating ingredients are zeolite particles of sizes from 10 to 100 μm, with the maximum of 25 μm, and zeolite particles of sizes from 100 to 1000 μm, with the biggest share of particles sized 300 μm. The bimodal distribution of the size of clinoptilolite grains is presented on Figure 6.

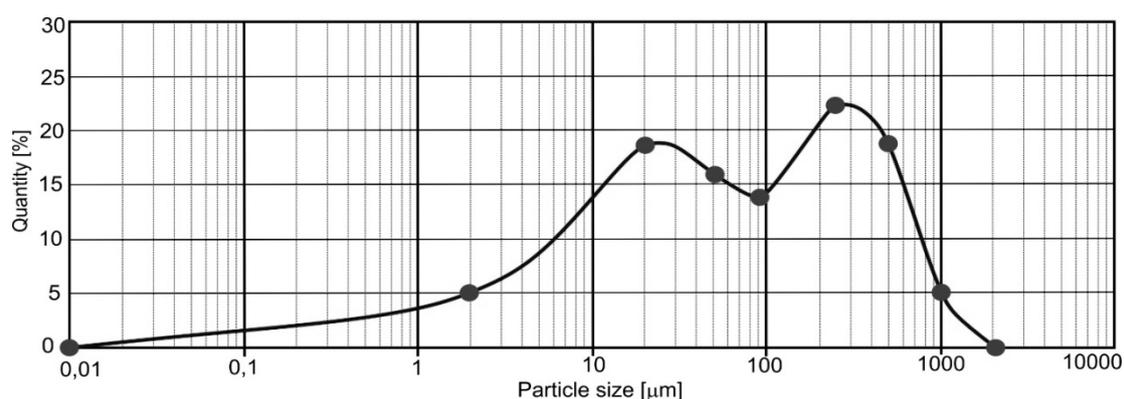


Figure 6. Bimodal distribution of clinoptilolite grain sizes.

The admixture used for the purposes of the selected base mixture containing exclusively aluminous cement consisting of clinoptilolite was introduced by means of a method consisting of a simple weight substitution of cement with 5 to 15% of clinoptilolite. The same dosage method of aluminosilicates was applied in the study [31].

#### 2.4. Properties of Designed Concrete Mixtures

Using traditional designing methods of concrete mixtures [32] and assuming restriction of mixture substrates to the commonly used cement and an appropriate addition of clinoptilolite, four series of samples were designed, differing only in the amount of added zeolite. Aluminous cement Górkal 70 was used as a binder. In each series, only aggregate obtained from waste ceramic whiteware, crushed into two aforescribed fractions, was used.

The ceramic material was crushed into two fractions of 0–4 mm and 4–8 mm, and subjected to a sieve analysis pursuant to [33]. As a result, the following percentage share of the particular fractions was obtained (related to the aggregate included in the designed compositions of concrete mixtures): 0–0.125 mm—1.14%, 0.125–0.25 mm—2.79%, 0.25–0.5 mm—6.29%, 0.5–1.0 mm—11.21%, 1.0–2.0 mm—21.79%, 2.0–4.0 mm—28.07% and 4.0–8.0 mm—28.57%. To compare, the crushing index of the aggregate of limestone equals 18–20%, granite—ca. 18%, quartzite sandstone—ca. 15% instead of gravel 12–16% [25].

To the base mixture, containing only aluminous cement and ceramic aggregate, clinoptilolite was added, adopting the method of replacing 5%, 10% or 15% of selected cement type with clinoptilolite. The samples were formed as cubes with a side length of 150 mm. A total of 120 pieces were made, with 30 pieces of each specified type. In addition, for the purposes of the bending strength testing, six samples of each designed group were prepared in the form of standard beam samples of 40 × 40 × 160 mm. All the prepared samples were cured in accordance with the requirements specified in the standard [34]. The weight compositions of the concrete mixtures used in the production of the concrete samples are specified in Table 2.

**Table 2.** Ingredients of the designed concrete mixtures.

Sample Designation	Z0	Z5	Z10	Z15
Aluminous cement Górkal 70 [kg/m <sup>3</sup> ]	488.00	463.60	439.20	414.80
Aggregate 0–4 mm [kg/m <sup>3</sup> ]	997.14	997.14	997.14	997.14
Aggregate 4–8 mm [kg/m <sup>3</sup> ]	398.86	398.86	398.86	398.86
Clinoptilolite [kg/m <sup>3</sup> ]	-	24.40	48.80	73.20
Water [L/m <sup>3</sup> ]	196.00	196.00	196.00	196.00

### 3. Test Results

#### 3.1. Testing of Compressive and Flexural Strength

Compressive testing of the concrete samples was performed with the use of the Controls Advantest 9 system for testing concrete and mortars according to the standards [35,36] at the Laboratory of Construction of the Faculty of Civil Engineering and Architecture of the Lublin University of Technology. The tests were based on cubic samples sized 150 × 150 × 150 mm, and were carried out after 7, 14, 28, 56 and 90 days following the date of their formation, and on 40 × 40 × 160 mm beam samples after a 28-day curing period. The universal testing machine used in the tests was furnished with three frames. The system works together with the tensometric bridge and enables readout of deformations at four measurement points. Additional inserts enable examination of the tensile strength of concrete elements, for example, standard cylinder or cubic elements or ready-made products, such as paving setts.

The results of the compressive testing are presented in Figure 7, and the results of the bending strength tests in Figure 8.

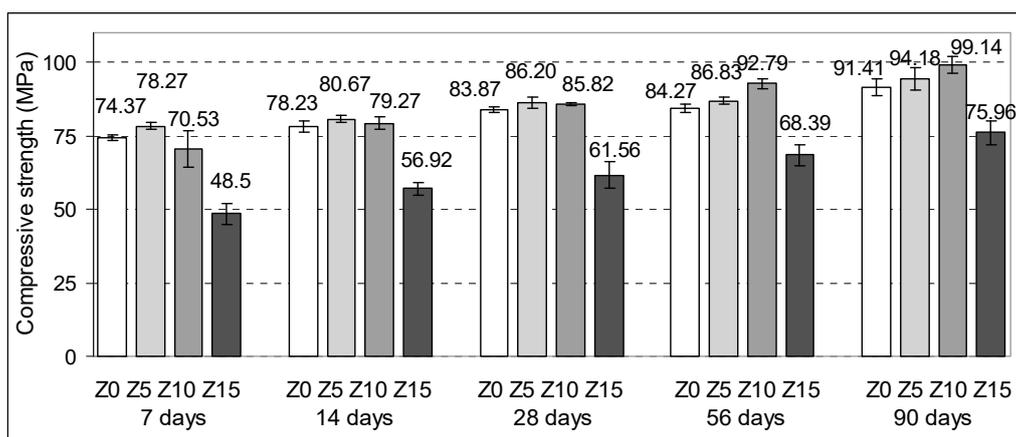


Figure 7. Compressive strength of the cubic samples including standard deviations.

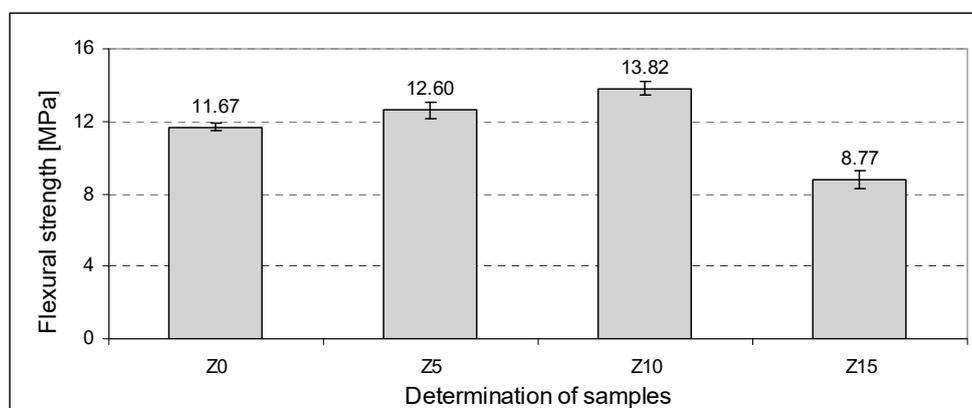


Figure 8. Flexural strength of the beam samples including standard deviations (28 days).

The test results showed that concrete with ceramic aggregate and aluminous cement gains high compressive strength already after 7 days following the sample production. It is caused by the type of the used cement, characterised by high initial strength; this phenomenon is described in the studies [32,37], among others. It was also proven that the replacement of 15% of cement with clinoptilolite decreased strength in all the test time periods. A decrease in average strength with regard to the remaining concrete mixtures was very pronounced and amounted to even 60% as compared to Z5 samples.

The highest average compressive strength in the period of 7–28 days was found in Z5 samples containing 5% of zeolite, while in the case of bending strength, the highest values were recorded for samples from the group Z10. As regards 56-day samples, the highest compressive strength was found in the samples Z10, and the trend was also confirmed for the period of 90 days.

### 3.2. Abrasion Resistance

To determine the application options of the designed concrete containing zeolite and recycled whiteware aggregate as additives, abrasion resistance tests were carried out. The testing was conducted pursuant to [38] and in accordance with appendix H. For the purposes of the testing, three cubic samples with the side length of  $(71.0 \pm 1.5)$  mm for each test were produced. The cubes were cut to the desired dimension from cubes with the side length of 100 mm on a circular saw. Prior to the testing, the samples were dried at a temperature of  $105^\circ\text{C}$  on the Böhme disc abrader until solid mass was obtained. During the testing, the disc was sprinkled with 20 g of corundum powder. Next, a sample was loaded with the force of  $294 \pm 3$  N and 16 abrasion cycles were carried out. Each abrasion cycle comprised 22 rotations of the disc. Afterwards, the sample was turned by  $90^\circ$ . On the whole, 16 cycles

(352 rotations) in accordance with the standard requirements were performed. The results of the height loss tests are presented in Figure 9.

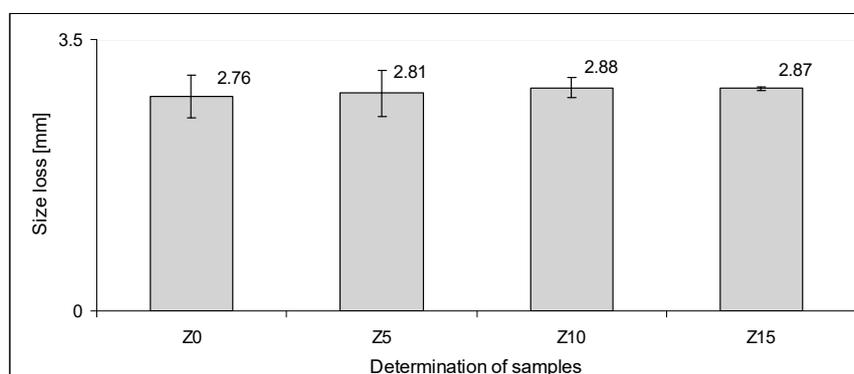


Figure 9. Comparison of the abrasion levels of the concrete samples.

The tests showed that the lowest abrasion level was recorded for the concrete Z0, that is, the one without the zeolite additive. As the amount of the additive increased, so increased the abrasion of the concrete. The highest abrasion level was recorded for the concrete Z10. It should be borne in mind that particular differences in concrete abrasion are quite insignificant and do not differ by more than 4%.

### 3.3. Depth of Water Penetration under Pressure

Testing of the depth of water penetration under pressure was carried out on cubic samples of a 150 mm side pursuant to the requirements of the standard [39]. For the purposes of the tests, six samples from each of the designed mixtures were produced. After the curing period, the samples were placed in the device and subjected to water pressure of  $(500 \pm 50)$  kPa for 72 h. After the expiry of the time period defined by the standard, the samples were removed and dried. Simultaneously, during the testing, the surfaces of the samples not subjected to the impact of water were observed. After the testing, the samples were split perpendicularly to the surface subjected to water. During the splitting and during the testing of the fractured surface, the sample was positioned in such a way that the surface of the water impact was at the bottom. The penetration depth was measured with rounding up to 1 mm. The obtained results are presented in Figure 10.

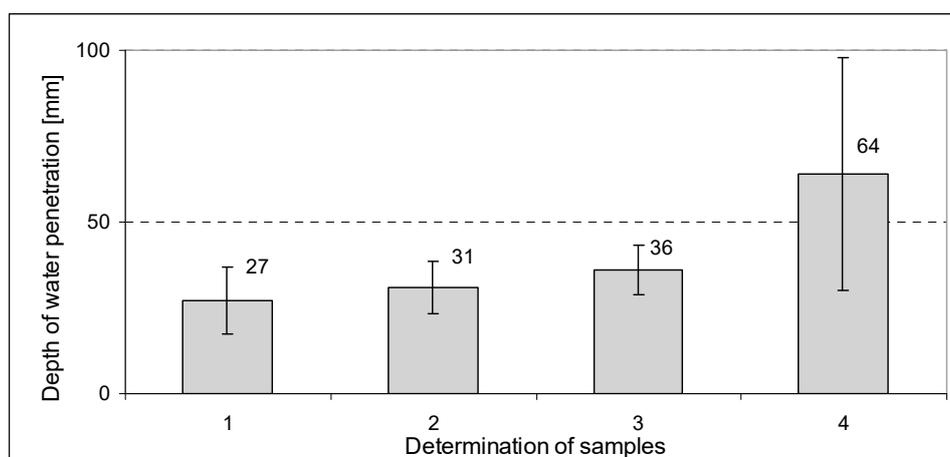


Figure 10. Comparison of the water penetration levels under pressure.

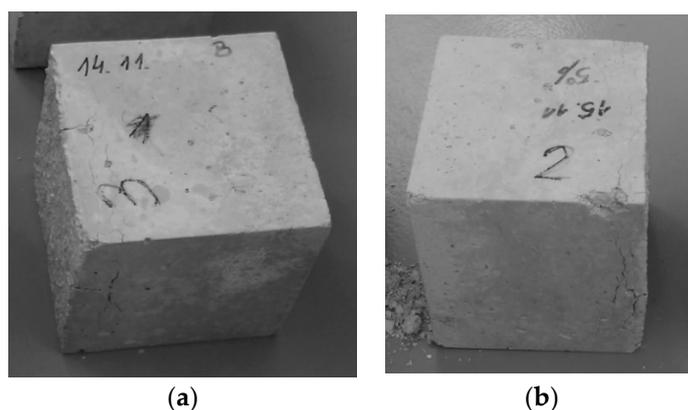
The studies showed that the lowest average level of water penetration was recorded for concrete without the addition of zeolite. As the addition of clinoptilolite grew, the level of water penetration

under pressure increased and was the highest in the case of the concrete Z15. In this case, the values of standard deviation were the highest, which indicates the variability of the obtained results.

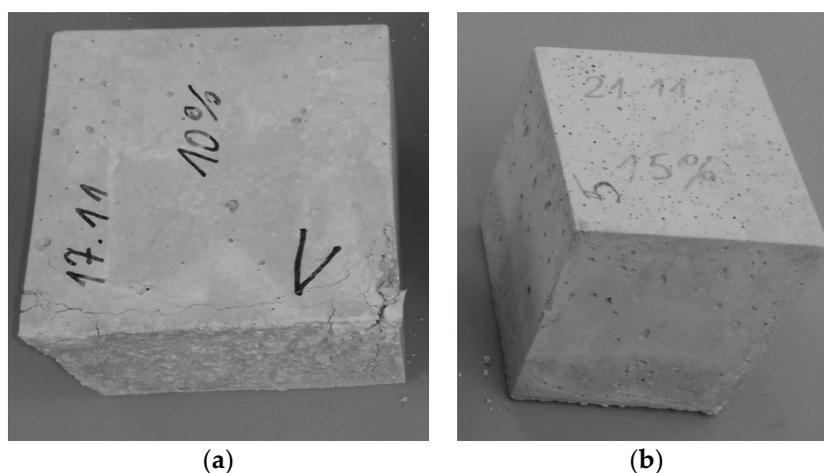
### 3.4. Frost Resistance of Concrete

Tests of frost resistance were carried out on cubic samples with the side length of 150 mm using the so-called “usual method”. The tests, performed pursuant to the standard [40], aimed to determine the frost impact considering the degree of concrete destruction as its compressive strength and external destruction determined by loss in the sample mass. For the period of the test, five samples from a given group were placed in a tub filled with water with a temperature of  $18 \pm 2$  °C. The remaining samples were placed in a chamber and subjected to freezing and thawing cycles. The freezing period at the temperature of  $-18 \pm 2$  °C lasted for minimum 4 h. Next, they were thawed in water at the temperature of  $+18 \pm 2$  °C from 2 to 4 h. The example cubic samples of the groups Z0, Z5, Z10, Z15 after the completion of freezing and thawing cycles are shown in Figures 11 and 12.

After the completion of the tests, a visual inspection of the samples was carried out. It was established that on the surface of the samples Z15 (with 15% of zeolite), no damage or disintegration was visible. On the other hand, in the case of the samples Z 5 and Z 10, there was a visible damage in the form of one or more cracks and delamination of small sample fragments. The most serious damage, not only to the surface, but also to the entire structure, such as cracking and larger delamination of fragments, was recorded for the samples Z0 (without the addition of zeolite).



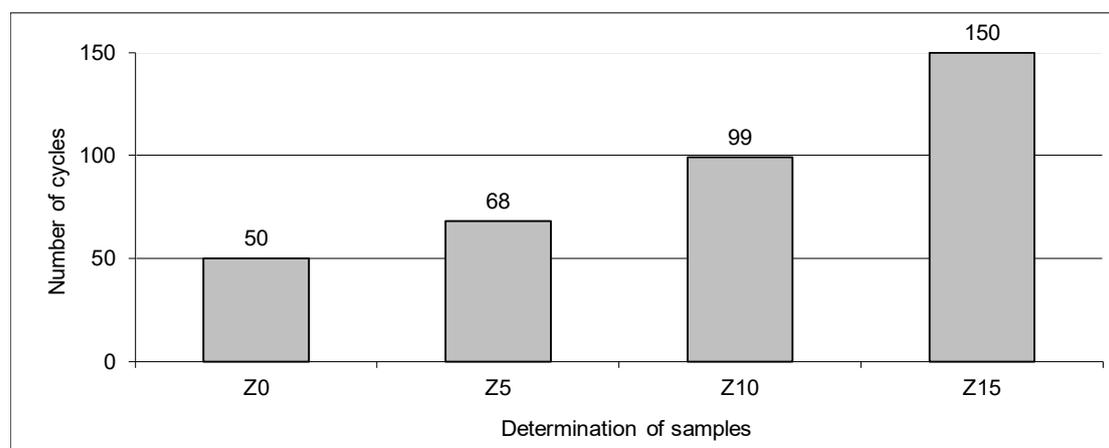
**Figure 11.** Example cubic samples after the completion of freezing and thawing cycles: (a) Z0, (b) Z5.



**Figure 12.** Example cubic samples after the completion of freezing and thawing cycles: (a) Z10, (b) Z15.

The numbers of cycles after which the samples demonstrated no cracking and the total concrete mass loss of the samples, such as destroyed corners and edges, chips, and so forth, did not exceed 5%

of the mass of the samples prior to the commencement of freezing/thawing cycles are presented in Figure 13.



**Figure 13.** Comparison of the numbers of the freezing/thawing cycles regarding the concrete samples without cracking and losses.

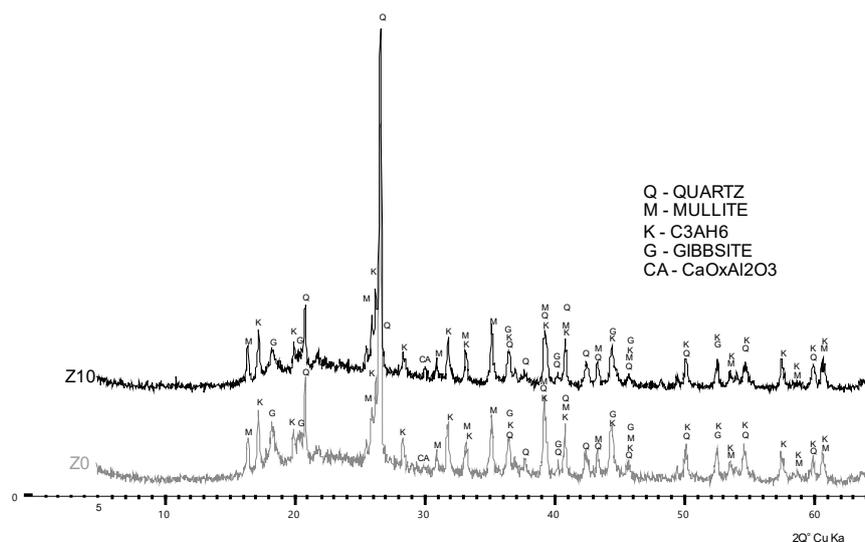
As the amount of clinoptilolite increased, the frost resistance of the designed concretes also tended to grow. Pursuant to the requirements of the standard [41], the group of the samples Z15 may be attributed the frost resistance degree of F150. As regards the concrete Z0, cracking and damage to the samples were already visible after 50 cycles, which indicates that such concrete should not be exposed to temperatures below 0 °C.

### 3.5. Phase Composition and the Microstructure of Concrete

The mineral composition of the designed concrete mixtures was determined by means of X-ray diffraction (XRD). Prior to the testing, the aggregate was crushed into dust with grading not larger than 5 µm. The analysis was performed with the use of the X-ray diffractometer Panalytical X'pert PRO MPD with the PW 3020 goniometer. As the source of the X-ray emission, the copper lamp Cu (CuKα = 1.54178 Å) was used. The diffraction data was processed by means of the X'PertHighscore software. The identification of mineral phases was based on the database PDF-2 Release 2010 formalised by JCPDS-ICDD. The diffractogram of the aggregate phase composition is shown in Figure 1.

To study the differences in the phases and microstructure, only the samples containing calcium aluminate cement with the phase composition Z10 and 10% of zeolite were selected. The selection of the sample groups depended on positive results of the tests of concrete compression strength, as well as the will to learn about the mechanisms generating such positive impacts. Mineral identification studies were first to be conducted with respect to the ceramic aggregate as such and calcium aluminate cement. Subsequently, a study of the concrete samples was performed taking into account basic samples.

The diffraction patterns of the phase composition of the concrete Z0 mix without zeolite and the mixture of Z10 with 10% of zeolite are presented in Figure 14.



**Figure 14.** Diffraction patterns of the mineral composition of (a) Z0 and (b) Z10 concrete mixtures.

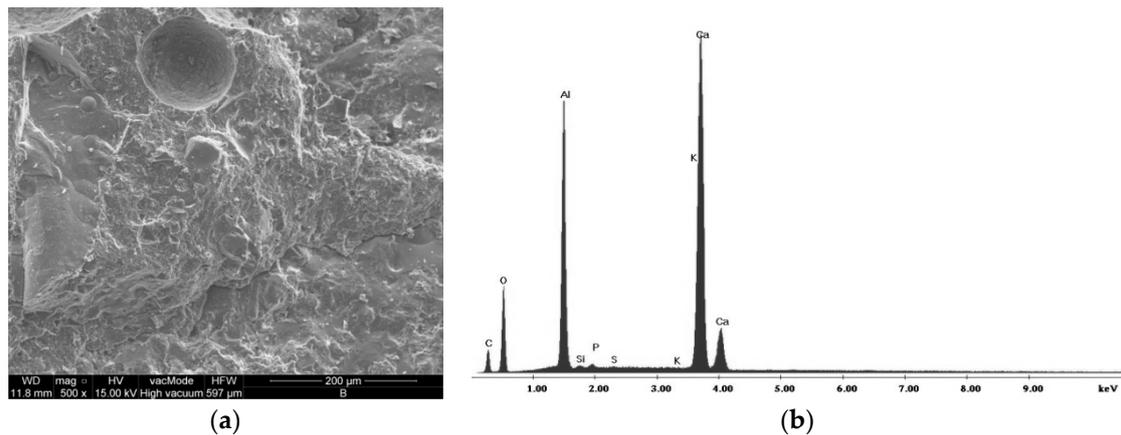
The phases of concretes, dependent on the used cement, are shown in Figure 15. In the minerals of calcium aluminate cement concretes, apart from the aggregate and residues of cement phases (CA and CA<sub>2</sub>), new crystalline phases are visible in the diffractograms—a result of the hydration process. As a result of the hydration process, in the samples of the concrete Z0 and Z10 appear hydrates, the chemical content of which is similar to C<sub>3</sub>AH<sub>6</sub> (katoite) and AH<sub>3</sub> (gibbsite). Katoite was recognized by the strongest reflections  $d_{hkl} = 0.5139; 0.3347; 0.3145; 0.2810; 0.2462; 0.2296; \text{ and } 0.2040 \text{ \AA}$ ; whereas gibbsite resulted in  $d_{hkl} = 0.3185; 0.3106; 0.2453; 0.2451; 0.2165; \text{ and } 0.2049 \text{ \AA}$ .

Figure 14, which specifies the diffraction patterns of the mixtures Z0 and Z10, shows changes in the slurry phase composition consisting in reduction of the amount of calcium hydroxide which results from the addition of zeolite; this positive impact is connected with the pozzolan properties of clinoptilolite.

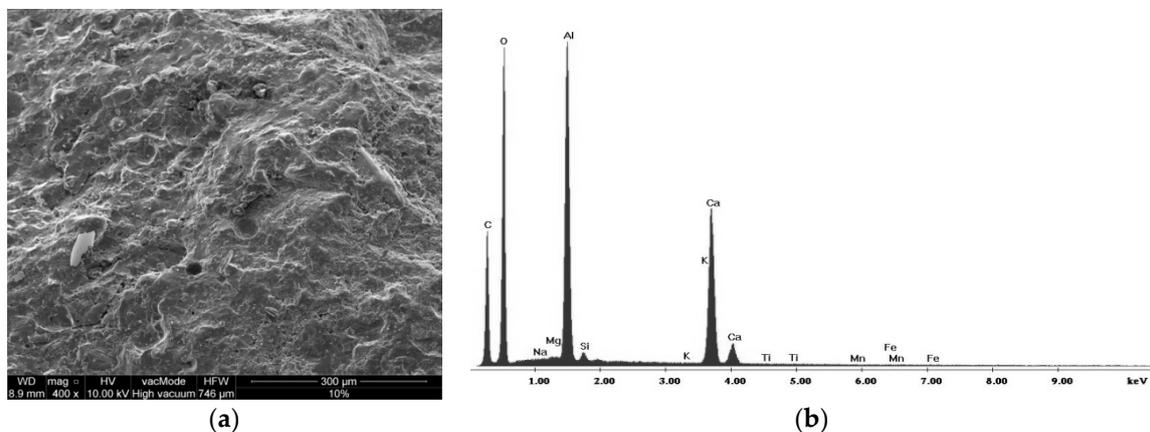
The microstructure of the examined materials was determined by means of Scanning Electron Microscope (SEM) Quanta 250 FEG by FEI (Hillsboro, OR, USA), equipped with a system of the chemical content analysis based on the X-ray energy dispersion using Energy Dispersive X-ray Spectroscopy (EDS, Panalytical, Almelo, The Netherlands) by EDAX. The obtained results are a semiquantitative analysis of chemical composition.

Testing carried out by means of a scanning electron microscope was performed on the model samples of Z0 without the addition of zeolite, and on the samples with the addition of zeolite Z10. The tests based on cubic samples were carried out 28 days after the date of their formation. SEM images of the sample microstructure were supplemented by EDS diagrams presenting the chemical composition of the studied samples.

Figures 15 and 16 present SEM images of the binder structure. In addition, the binders were subjected to a test of chemical composition SEM-EDS. Table 3 presents analyses of the composition of the reference concrete Z0, and with added zeolite Z10, conducted on the basis of energy dispersion (EDS results from the entire testing area).



**Figure 15.** (a) View of the microstructure of the concrete Z0 mixture binder, 500x enlargement. (b) EDS elemental analysis of the area visible in the image.



**Figure 16.** (a) View of the microstructure of the concrete Z10 mixture binder, 400x enlargement. (b) EDS elemental analysis of the area visible in the image.

**Table 3.** Chemical ingredients of the binders in the designed mixtures.

Determination	Contents of Compounds [%]							
	Al <sub>2</sub> O <sub>5</sub>	CaO	SiO <sub>2</sub>	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O
Z0	48.23	50.45	1.05	-	-	0.25	-	-
Z10	66.83	30.24	2.12	0.56	0.24	-	-	-

The content of CaO in the tested concrete samples decreased considerably, practically “proportionally” to the added zeolite. The highest content of calcium oxide was found in the reference samples Z0 (without added zeolite) as compared to the samples Z10 (its contents are 40% higher). As zeolite was added, the porosity of the binder microstructures of the designed concrete mixtures tended to decrease. A positive impact was possible thanks to the pozzolanic properties of clinoptilolite and related changes in the chemical composition of slurry consisting in the reduction of the amount of calcium oxide.

According to Ahmadi and Shekarchi [42], the use of zeolite in the amount of up to 10% in the cement–zeolite binder mass may, however, result in a more gas-tight microstructure than when silica fume is used.

The high strength of a mixture with both zeolite and silica fume (10%) mortars can also be related to the uniform distribution of pozzolan particles in the mixture, which additionally seals the mortar microstructure [43,44].

#### 4. Conclusions

The results of the tests carried out are as follows:

- Compressive strength tests have demonstrated the beneficial effect of replacing aluminous cement with the addition of zeolite from the zeolite tuff deposit in Sokyrnytsya (Ukraine). The use of zeolite in the amount of 5% results in an increase in compressive concrete strength by a few percent in the maturing period of 7–28 days as compared to the control samples. On the other hand, the addition of zeolite in the amount of 10% causes an increase in compressive strength by approx. 10% in a later period of maturation of 56 days and more. Increasing the additive to 15% results in a significant reduction in the compressive strength of the samples (up to 60%) in all studied periods of time.
- The highest value of flexural strength has been obtained for the samples of the group Z10, showing an 18% increase in the strength value in relation to the base samples.
- Abrasion tests have proven that, despite a slight increase in the average abrasiveness of concretes with the addition of zeolite (up to a maximum of 4%) with respect to the control samples, the designed concretes are abrasion-resistant and can even be used as surface concretes.
- Significantly worse results have been obtained in the tests of the depth of water penetration under pressure. The increase in the zeolite addition causes an increase in the depth of water penetration under pressure. In the case of Z15 concrete, it is over twice as high as the reference samples Z0.
- In the concrete frost resistance tests, the best results have been obtained for the concrete Z15, which qualifies it for a high degree of frost resistance, F150.
- X-ray diffraction (XRD) has demonstrated changes in the phase composition of the mixtures Z0 and Z10, consisting in reduction of calcium hydroxide. It results from the peculiar properties of zeolite.
- Microscopic examinations (SEM) of the samples Z5 and Z10 have shown good adhesion of the grains of ceramic aggregate and cement binder.
- Thanks to the use of aluminous cement and a zeolite additive, an increase in the initial compressive strength has been obtained. The previous research [45] and data found in the literature [6–9] show that samples with Portland cement and zeolite do not demonstrate such a material feature.
- A partial substitution of cement with a natural mineral such as zeolite in a concrete mix has a positive influence on the environment through limiting the effects of cement production, while the use of waste ceramic aggregate in concrete involves managing large amounts of waste from ceramic sanitary ware factories and limiting the extraction of natural aggregates.

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