Application of Natural Mineral Additives in Construction

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Abstract. The article concerns the idea of using selected mineral additives in the pavement quality concrete composition. The basis of the research paper was the modification of cement concrete intended for airfield pavements. The application of the additives: metakaolinite and natural zeolite was suggested. Analyses included the assessment of basic physical properties of modifiers. Screening analysis, assessment of micro structure and chemical microanalysis were conducted in case of these materials. The influence of the applied additives on the change of concrete mix parameters was also presented. The impact of zeolite and metakaolinite on the mix density, oxygen content and consistency class was analysed. The influence of modifiers on physical and mechanical changes of the hardened cement concrete was discussed (concrete density, compressive strength and bending strength during fracturing) in diversified research periods. The impact of the applied additives on the changes of internal structure of cement concrete was discussed. Observation of concrete micro structure was conducted using the scanning electron microscope. According to the obtained lab test results, parameters of the applied modifiers and their influence on changes of internal structure of cement concrete are reflected in the increase of mechanical properties of pavement quality concrete. The increase of compressive and bending strength in case of all analysed research periods was proved.

1. Introduction

According to the analysis of the obtained laboratory test results, the article suggests using natural mineral additives, which are distinguished by puzzolan characteristics, in the composition of cement concrete intended for airfield pavements. The purpose of modification of concrete mix composition was to reduce the quantity of the dozed cement in concrete capacity unit, and in consequence to reduce the amount of emitted CO₂. According to the principle of sustainable development, pavement quality concrete is referred to more often. [3, 5]. With reference to pavement, the definition of sustainable development [14], should be distinguished by low energy expenditure, low pollutant emission and the environmentally friendly structure. Taking into consideration the aforementioned factors, alternative solutions should be searched which will partially reduce cement consumption, without reducing the quality and durability of the future structures.

Metakaolinite and zeolite from natural puzzolan group were selected for experimental research. These materials, thanks to fragmentation similar to cement granulation, react in water environment with free calcium hydroxide (Ca(OH)₂) producing hydrated calcium silicates (CSH).

The purpose of the research was the evaluation of basic physical properties of the applied modifiers in the form of zeolite and metakaolinite with reference to cement properties. The influence of the applied
materials on the change of basic mechanical properties was also assessed, i.e. compressive strength and fracture strength of the modified cement concrete with reference to airfield pavement application.

2. Materials

The scope of laboratory tests with regard to base materials included the analysis of grain size distribution, observation of internal structure and chemical analysis. Cement CEM I 42.5 N-MSR/NA was selected for the research, as the most frequently used material for airfield pavements constructions. As cement substitute, metakaolinite and zeolite were also used in concrete mix. In case of these materials, analogical scope of laboratory tests was conducted. The remaining components of concrete mix (coarse aggregate, fine aggregate, water and admixtures) were selected in accordance with the requirements of the applicable standard [18] and remained unchanged, regardless of the dozed modifier.

2.1. Cement

Cement, as the basic component of concrete composite, combined with water acts as binder which combines all the components. To conduct laboratory tests, low-alkali cement intended for the bridge and airfield structures was used CEM I 42,5 N-MSR/NA, in accordance with the requirements [18]. Pursuant to the obtained test results it was proved that the analysed cement was distinguished by the grain size between 0 and 100 μm (Figure 1).

![Figure 1. Screening curve of the analysed cement with the grain size distribution function](image)

Based on the observation by means of scanning electron microscope Quanta Feg 250, it was proved that cement grains are of irregular, sharp-edged shape of average dimensions of 4μm. In order to determine basic elements in the examined cement, chemical microanalysis was conducted. Based on the obtained results, Ca, O, Si, C, Al, Mg, Fe and S elements were found in cement composition. (Figure 2).

![Figure 2. Structure of the examined cement: a) according to macro scale, b) SEM image and c) image of chemical microanalysis](image)

Based on X-ray diffraction analysis results, the following crystalline components were distinguished in the examined cement: alite, belite, tricalcium aluminate, tetracalcium aluminoferrite, gypsum, bassanite, anhydrite, free CaO and MgO and calcite. Evaluation of phase composition of the examined cement, according to the Instruction ITB No. 419 [16] proved that their alite indicators correspond to the assumed cement standard CEM I.
2.2. Metakaolinite
Metakaolinite is the highly chemically reactive material, which is formed as a result of roasting of natural kaolinite in temperature from 700°C to 900°C. [10] This material has puzzolan properties thanks to dehydroxylation of kaolinite. It is formed of silicon and oxygen coat with the attached gibbsyt coat so that one atom of oxygen of tetrahedron [SiO₄] is shared by octahedron in gibbsyt coat AlO(OH)₂ forming double-layer packages. General formula of metakolinite Al₂[Si₂O₅](OH)₄ [9]. Metakaolinite of extensive specific surface area influences also rheology of young concrete. Modification of concrete mix using metakaolinite increases thixotropy properties of concrete resulting in the reduction of cement grout in the course of concrete mix compaction. Eventually, the smoother surface of concrete can be obtained. [9] Reducing calcium hydroxide contents formed during hydration of cement, partially responsible for reducing of concrete durability, causes the improvement of concrete resistance to sulphate influence and alkali-aggregate reactivity. This results from increasing the contents of phase C-S-H as metakaolinite product of Ca(OH)₂.[10] Kaolin applied for laboratory tests after the roasting process, was finely ground in a ball mill, which allowed to achieve grain size distribution between 0 and 500 μm (Figure 3).

Figure 3. Screening curve of the analysed metakaolinite with the grain size distribution function

The analysed metakaolinite was intended for the observation by means of scanning electron microscope Quanta Feg 250. According to SEM observations it was proved that metakaolinite grains are of irregular shape. Based on the chemical microanalysis of the analysed metakaolinite, the occurrence of the following elements, i.e. O, Si, Fe, Al, Ca, K was proved (Figure 4).

Figure 4. Structure of the examined metakaolinite: a) according to macro scale, b) SEM image of cement grain from SEM and c) image of chemical microanalysis

2.3. Zeolite
The source of natural zeolite formation in the nature was settlement of volcanic ash and then reaction with lake slats. [2]. These minerals have diversified and loose structure which contains huge voids and nano channels. Total volume of voids is between 24-32%. [4]. Particular physical properties of zeolite are identified by their three-dimensional crystalline structure. Basic system unit are tetrahedrons distinguished by variable silicon-aluminium ratio. Zeolite - klinoptilolite which occurs in large in nature was subject to laboratory tests. The material from eastern Slovakia - Nižný Hrabovec area was analysed.
Obtained in the form of mineral and then fine-ground modifier reached grain-size distribution from 0 to 100 μm (Figure 5).

Based on SEM observation, it was proved that klinoptilolite grains are of irregular. In order to determine basic elements in the analysed material, chemical microanalysis was conducted. According to the obtained results, there was O, Si, Al, K, Ca, Fe, Mg, Na in zeolite composition. (Figure 6).

3. Methodology and test results

The experiment assumed to perform three series of concrete. The first series was reference concrete (R), in accordance with the requirements of [18]. Two consecutive series included concrete with partial cement substitute in the form of metakaolinite (series M) and zeolite (series Z). The composite included the following basic materials: natural sand fraction 0/2 mm (Niedzieliska), basalt chippings fraction 2/8 mm and 8/16 mm (Gracze), admixture reducing the amount of water based on calcium lignosulfonate, aerating admixture based on synthetic tensides, pipeline water which complies with requirements of [20] maintaining water-cement ratio at 0,4 – in accordance with the requirements of [18]. Aggregate grading composition of mix series R, M and Z was selected according to the guidelines of [18] taking into consideration limit curves of good grain size distribution (Figure 7).
Quantity selection of the remaining components (table 1) was based on experimental methods maintaining the consistency of reference mix at S1 level and taking into consideration the exposure class XF4, with the air amount between 4.5-5.5%. Mineral additives in the form of zeolite and metakaolinite were used in the amount of 15%, as partial cement substitutes.

Table 1. Compositions of the designed mixes of the following series R, M and Z

| Components        | R   [kg/m³] | M   [kg/m³] | Z   [kg/m³] |
|-------------------|----------|-----------|-----------|
| Cement            | 370.00   | 314.5     | 314.5     |
| Mineral additives | -        | 55.2      | -         |
| Aggregate 0/2mm   | 598.39   | 598.39    | 598.39    |
| Aggregate 2/8mm   | 864.34   | 864.34    | 864.34    |
| Aggregate 8/16mm  | 753.53   | 753.53    | 753.53    |
| Water             | 148.00   | 148.00    | 148.00    |
| Plasticizer       | 2.59     | 2.59      | 2.59      |
| Aerating agent    | 1.67     | 1.67      | 1.67      |

3.1. Evaluation of the influence of selected modifiers on concrete mix parameters

In order to evaluate the influence of selected modifiers on the change of concrete mix parameters the tests were conducted including the following: (table 2): mix density using cylinder of 8 dm³ capacity according to [22], consistency using concrete slump method according to [21], air contents using manometer method according to [23]. Pursuant to the obtained laboratory test results, it was proved that the suggested mineral additives are distinguished by finer grading than cement. This feature influenced the increase of density of modified mix by 3% with respect to the reference mix. Increased density of mix ensures more tight cement matrix. Consequently, it may contribute to the increased resistance of the hardened cement concrete to aggressive environmental factors (e.g. anti-slip agents or those resulting from aircrafts operation).

Table 2. Results of the basic concrete mix parameters

| Mix parameters | R   | M   | Z   |
|----------------|-----|-----|-----|
| Density        | 2530| 2600| 2600|
| Consistency    | 20  | 5   | 5   |
| Air contents   | 5,5 | 4,0 | 3,5 |

Smaller grading of the applied modifiers requires using additional amount of plasticizer in order to obtain the assumed consistency class. This refers to extension of specific area of fine particles. Positive aspect of this phenomenon is the absence of mix segregation during transport and incorporation. Mineral additive plays the role of filling material and using the sliding formwork may prevent falling off slab edges after paver operation. [13].

The concerning phenomenon resulting from the application of modifiers is the reduction of air contents in the fresh mix, which may be reflected in the decreased frost resistance of hardened concrete. Reduction of air quantity using natural zeolite is particularly visible, however porous structure of zeolite grains, which do not react with puzzolan, may play the role of air entraining agent. This conclusion is consistent with the test results of the author. [12]. This aspect, due to the essence of concrete durability in airfield concrete pavement structures is the subject of further analyses.
However, it should be emphasized that the complete assessment of the influence of applied materials on the porosity characteristics and, as a consequence, frost resistance of concrete, should be extended by hardened concrete tests. Only then, the conclusions concerning the influence of the modifier on air entraining of concrete and frost resistance thereof, will be complete.

3.2. The evaluation of influence of the selected modifiers on the selected physical and mechanical parameters of hardened concrete

The purpose of the research was the evaluation of influence of the selected modifiers on the change of hardened concrete parameters over time. Prepared concrete mix of series R, M and Z after concrete pouring (cubic forms 150x150x150 mm, in accordance with the standard [23]) was subject to standard curing [25] for the assumed research periods (1, 3, 7, 28 days). Additionally, hardened concrete tests were conducted after the extended curing period up to 90 days (samples were stored from 28th day in air-dried conditions in average air temperature 22.7°C and the humidity...%). Hardened concretes were used in destructive testing, their volumetric density was specified according to [28], their ultimate compressive strength according to [26] during diversified research periods. Based on the obtained laboratory test results, concrete types containing mineral additives were of slightly higher volumetric density (Figure 8).

Obtained results of average compressive strength, in the event of using natural mineral additives, prove their positive impact on the examined parameter. This influence was disclosed both during the initial period of concrete setting and after the extended curing period up to 90 days. It should be noticed that all of the designed concrete types achieved the design class C30/37. Using metakaolinite and zeolite in the mix composition influences raising of the obtained concrete class from C30/37 to C35/45 in case of concretes of M series and to C40/50 in case of concrete of Z series. It should be mentioned that raising concrete resistance class was equivalent to reducing cement contents at the same time.

According to the obtained results it was proved that the replacement of 15% of cement with the modifier in the form of metakaolinite contributes to the increase of average concrete compressive strength in comparison to reference concrete. The following observations were made: increase of average compressive strength by 25% after 1 day, 10.8% after 3 days, 25.4% after 7 days, 18.5% after 28 days and 28.9% after 90 days of curing. The most significant increase in resistance was observed after the extended curing period, which is caused by the properties of the modifier itself and its influence on changes in internal microstructure of the formed concrete composite.

Figure 8. Average hardened concrete density of series R, M and Z during diversified curing periods
In a consequence of replacing 15% of cement with the suggested zeolite additive, the increase of average concrete compressive strength in comparison to the reference concrete was proved. Increase in the strength was 48.4% after 1 day, after 3 days 1.5%, after 7 days 9.3%, after 28 days 36.6%, and after 90 days by 30.7%. The most significant increase of strength was observed after 28 days of standard curing. Modifier performance and the internal structure of the newly formed concrete composite significantly influenced the increase of strength. Series of concrete types R, M and Z were subject to the analysis of the influence of applied modifiers on average tensile strength while fracturing. The test was conducted using samples curing in standard conditions for 28 days.

Figure 9. Average compressive strength of hardened concrete types of series R, M and Z after the assumed curing periods

According to the obtained laboratory test results, it was proved that replacing 15% of cement with mineral additive influences the increase of the analysed feature. In case of metakaolinite additive, the increase in strength is 12%, while in case of zeolite it increases up to 22%.

3.3. Evaluation of the influence of selected modifiers on hardened concrete microstructure

In order to assess the influence of the applied modifiers on the change of internal structure of concrete composite, the following concrete types of R, M and Z series were subject to SEM observations. At this stage of the research the scanning electron microscope of Quanta FEG 250 type was used.
Preparations were made of concrete samples, each of the surface of at least 100 mm². Template micro pictures obtained during the observations were presented in Figure 11.

![Figure 11. Internal microstructure of concrete types: a) series R, b) series Z](image)

The internal structure of concrete of R series is distinguished by non-continuous contact areas between aggregate grains and cement matrix. Cement matrix, in case of this type of concrete, is consistent and crystallization of hydrated calcium silicate occurs in fine-fibrous form. Internal walls of air voids undergo cracking of the width up to 9μm.

Metakaolinite contains active forms of aluminium oxides and silicon monoxides which react with free calcium hydroxide Ca(OH)₂. The formed products favourably influence concrete micro structure and contribute to the increase of concrete resistance parameters.

According to the conducted SEM observations it was proved that the applied zeolite contributes to the change of internal structure of cement matrix. Hydrated calcium silicates, in case of concrete of Z series, occurs in the fine-grained form. Crystallization of ettringite with the length of single crystals of which is up to 6μm, occurs in cement matrix. Contact areas between aggregate grains and cement matrix are continuous. Crystallization of ettringite (length up to 3μm) and cracked walls of air void interior were proved. Zeolite grains are covered with fine ettringite crystals.

### 4. Conclusions

According to the conducted laboratory tests, the following conclusions have been reached:

- cement composition contains Ca, O, Si, C, Al, Fe, Mg and S, metakaolinite contains O, Si, Fe, Al, Ca and K, zeolite contains O, Si, Al, K, Ca, Fe, Mg and Na;
- additives in the form of metakaolinite and zeolite used in concrete mix cause insignificant increase of volumetric density of hardened concrete and consequently sealing of internal structure;
- applied modifiers favourably affect the changes of internal structure of concrete composite (contact areas between aggregate grains and cement matrix, crystallization of cement matrix, air void);
- additives used in concrete mix contribute to the increase of concrete ultimate compressive strength after standard curing period by 18.5% in case of metakaolinite and by 36.6% in case of zeolite. It is equivalent to raising the class of the obtained concrete with regard to the design concrete by one (C30/37 → C35/45) and two (C30/37 → C40/50);
- metakaolinite additive used in concrete mix composition causes the increase of tensile strength during fracturing by 12%, whereas zeolite additive by 22%;
- suggested additives allow for the reduction of cement quantity in mix composition for pavement quality concrete, at the same time increasing mechanical parameters of hardened concrete, which complies with the assumptions of sustainable development.

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