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THE EFFECT OF A COMPLEX POZZOLANIC ADDITIVE CONSISTING OF MILLED GLASS AND METAKAOLIN ON THE DEGRADATION OF A CEMENTITIOUS COMPOSITE WITH GROUND WASTE GLASS CAUSED BY ALKALI-SILICA REACTION

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This paper investigates the effect of partial replacement of cement by milled glass (MS), metakaolin (MK), and their mixture and partial replacement of sand by crushed glass (TS)on the physical and mechanical properties of a cementitious composite, as well as on the resistance of the composite to degradation caused by alkali-silica reaction (ASR). After 28 and 56 days of curing, the highest improvement in the mechanical properties was observed in the batches of specimens with the MS, MK and their mixture. The physical and mechanical properties of specimens with partially replaced sand to TS also deteriorated the least (the lowest expansion 0.02 %) with the application of the MS and MK mixture after 56 days of exposure to alkaline attack. XRD and microstructural analyses have shown that the reduction in expansion is due to the higher content of hydration products, as well as to the denser contact zone between the aggregate and the cementitious matrix.

INTRODUCTION

Concrete is the most commonly used material in the construction sector. Cement, which is the main component of concrete composite, is produced at a rate of around 4 billion tonnes per year [1]. The increase in the consumption of natural resources and energy correlates with population growth. The increasing growth and consumption raise concerns about the exhaustion of natural resources, waste generation and the emission of harmful gases into the environment [2-5]. The demand for alternative aggregates in cementitious composites in the construction industry is increasing day by day, the use of river sand as fine aggregate is leading to the depletion of natural resources and the drop in groundwater levels. For these reasons, the aim is to reduce the use of pure cement in the construction industry and to discover supplementary cementitious materials (SCMs) [6]. Given the major environmental impact of cement manufacturing, it is necessary to develop alternative binders for the production of concrete [7]. Generally, pozzolans are used as cement replacements rather than as cement additives. Pozzolans are silicate-based materials. Therefore, when cement is replaced with different amounts of pozzolans, the content of calcium oxide diminishes and the content of silica increases. The pozzolans react with calcium hydroxide (CH) produced by during cement hydration to form additional cementitious material, namely calcium silicate hydrate (C-S-H) [8].

The use of waste glass (WG) in concrete has been studied in the United States and Europe since 1980. WG can be used in concrete manufacturing as a fine aggregate to replace part of sand with crushed glass, or as an additional cementitious material to replace cement with milled glass. In the first case, the glass has both positive and negative effect on the properties of concrete [9]. Waste glass, which consists mainly of amorphous SiO_2, Na_2O and CaO, is a stable, non-biodegradable material [10]. The recovery of these substances in cementitious systems contributes to environment protection, as industrial and household glass waste is mostly landfilled. However, the recycling of waste glass in cementitious systems can lead to degradation of concrete due to alkali-silica reaction. Alkali-silica reactions (ASR) are usually caused by the reaction between the alkali present in the cement and the silica present in the aggregates. These reactions lead to expansion that deteriorates the mechanical properties of concrete. Researchers have identified three main factors of ASR in concrete: alkalis in the solution in the pore solution, reactive amorphous or non-crystallised silica in some aggregates, and water [11]. Alkali-driven degradation of concrete is the delamination of a concrete structure caused by the expansion of calcium hydrosilicate gel, a product of ASR in the mix [12].

Researchers found [13-14] that the types of aggregates and the distribution of pore sizes and types influence the expansion of concrete. In order to improve the environmental situation, attempts have been made to use crushed glass as fine aggregate instead of sand [15]. Milled glass can be used as an additive to replacing part of the cement in concrete mixes. The colour of the glass also influences the development of ASR. For example, clear soda lime glass with sodium has been found to be the most reactive followed by less reactive brown glass [16].

There are two types of alkali-aggregate reactions: alkali-silica reaction (ASR) and the alkali-carbonate reaction (ACR). ASR is much more common than ACR in the world [17]. ASR takes place between reactive silica in certain types of aggregates and alkaline solutions in concrete micropores. The main sources of alkali are the binder, aggregates and the surrounding environment. Alkali formed from alkali metal ions react with water to form soluble alkali hydroxide compounds [18]. Thus, the main concern for the use of waste glass in concrete is the chemical reaction between silica-containing glass particles and the alkali present in the concrete pore solution, i.e., the alkali silica reaction (ASR). This reaction can be very detrimental to the stability of the concrete unless appropriate precautions are taken to minimise its effects. Such precautions include adding a suitable pozzolanic material such as fly ash, silica fume or ground blast furnace slag to the concrete mix in appropriate proportions [19].

Fine glass particles tend to have pozzolanic activity, which is beneficial to concrete, whereas coarse particles tend to be detrimental to concrete due to the alkaline reaction of silica fume (ASR). Although the use of milled glass particles is an effective solution for re-using waste glass in concrete, the milling of glass is expensive, as it takes several hours to mill the glass to the sufficient fineness that is almost equivalent to the fineness of cement [20]. There are studies where the use of waste glass in concrete is investigated. Authors have reported that a higher amount of waste glass used as a coarse aggregate reduced the mechanical properties of concrete, in particular due to the weak bond between the matrix and the aggregate [21]. ASR effects can be reduced by using finely milled glass as cement replacement or even as aggregate [22]. The efficiency of this blending depends on the replacement ratio, which can be up to 20 % of glass content in the mix. Recently, metakaolin is one of the most commonly used pozzolanic materials. Metakaolin helps to reduce $CaOH_2$ formed during cement hydration and related to poor durability of concrete. This makes the concrete more resistant to sulphate attack and reduces the effects of alkali-silica reactions [23-24]. A study by Poon et al. on the effect of metakaolin content on hardened concrete showed that a higher amount of MC in concrete increases the strength and reduces the porosity of concrete [25].

Metakaolin is produced at lower temperature (600 °C – 900 °C) compared to Portland cement (1450 °C) [26-27]. Lower calcination temperature requires less energy and thus reduces the binder production cost. There are few studies on the individual and combined effects of metakaolin and milled glass as a cement substitute in concrete. It was reported that the combined performance of the two pozzolanic additives mixed with cement was better than the performance of each material used separately [28]. Researchers tested the durability of green self-compacting concrete that incorporated recycled cathode ray tube glass and metakaolin [29]. Natural sand was substituted with recycled glass at 0, 10, 20, 30, 40, and 50 per cent by weight of cement in various concrete compositions, while the cement was partially replaced with metakaolin at replacement ratios of 5, 10, and 15 per cent by weight. After 90 days of curing, the compressive strength of concrete specimens containing 10 % of metakaolin and 50 % of recycled glass improved by 16 % whereas the ASR limit was 0.1 %.

The effects of the use of ground waste glass in combination with either milled waste glass or metakaolin, as well as the use of the mixture of milled glass and metakaolin, on mortar or concrete properties, including ASR caused damage, have not been widely studied. This paper presents a research designed to evaluate the mechanical and ASR related performance of the mortar incorporating crushed waste glass as an aggregate and milled waste glass and metakaolin as cement substitutes in order to maximize the possibility of recycling a higher amount of waste in construction materials and to improve the resistance of construction materials to ASR. The current research into glass and metakaolin waste recycling and its reuse as SCMs can significantly reduce the deleterious effect of ASR and has beneficial ecological and economic effects.

EXPERIMENTAL

Materials and methods of testing

Portland cement CEM I 42.5 R, milled glass, and metakaolin were used for the tests. The particle density of milled glass was 2500 $kg \cdot m^{-3}$, bulk density was 850 $kg\ m^{-3}$. Metakaolin particle density was 2147 $kg \cdot m^{-3}$, bulk density was 600 $kg \cdot m^{-3}$. Table 1 presents chemical compositions of cement, milled glass and metakaolin. The pozzolanic activity of milled glass (560 $mg \cdot g^{-1}$) was found to be lower compared to the activity of metakaolin (927 $mg \cdot g^{-1}$). Figure 1 shows the X-ray diagrams of glass (a) and metakaolin (b). The curves of amorphous silica dioxide are visible in milled glass X-ray diagram. The XRD analysis of metakaolin showed the presence of quartz, kaolinite, illite and microcline.

Figure 2 presents the results of the SEM test performed on the milled waste glass and metakaolin.

Table 1. Chemical composition of cement, milled glass and metakaolin.

SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	SO_3	At_2 About	TiO_2	MgO	Other
			Chemical composition of cement (%)						
20.76	6.12	3.37	63.50	1.00	0.8	0.3	–	–	4.45
			Chemical composition of milled glass (%)						
68.15	12.18	1.30	3.95	2.80	–	0.75	0.20	0.90	9.77
			Chemical composition of metakaolin (%)						
50.6	34.0	0.74	2.49	0.7	0.07	10.1	0.37	0.59	0.34

The particles of milled waste glass seen in Figure 2a have an irregular shape and an average size of approx. 15 µm. Figure 2b clearly shows metakaolin plates with an average size of 10 µm.

Sand of fraction 0/4 with a particle density of 2488 $kg\cdot m^{-3}$ and a bulk density of 1643 $kg\cdot m^{-3}$ was used for the tests.

Crushed glass of fraction 0/4, particle density of 2294 $kg\cdot m^{-3}$, and a bulk density of 1204 $kg\cdot m^{-3}$ was used to replace 25 % of the sand in the cementitious composite.

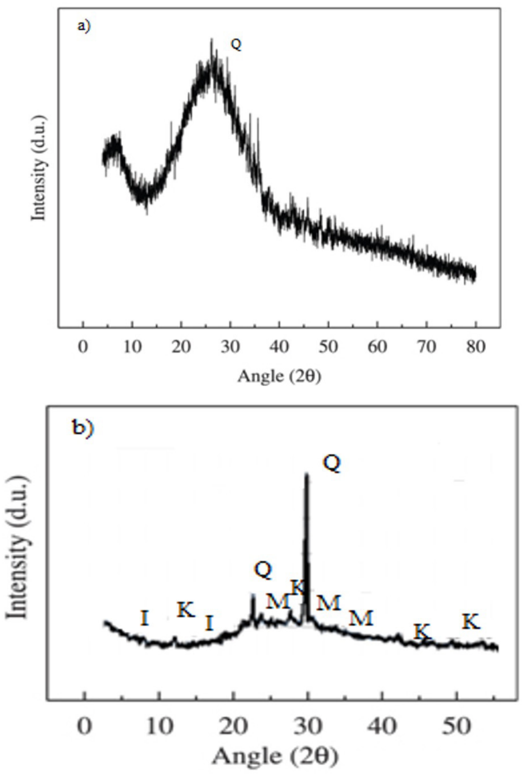

Figure 1. a) XRD of milled glass: Q - quartz b) XRD of metakaolin: M - microcline, I - illite, K - kaolin, Q - quartz.

The compositions of specimens formed from cement composite are presented in Table 2. The specimens were made by replacing some of the cement with ground waste glass and metakaolin. In the cement composite, 25 % of sand was replaced by crushed glass. The water-to-cement (W/B) ratio of 0.46 was kept constant for all the specimens.

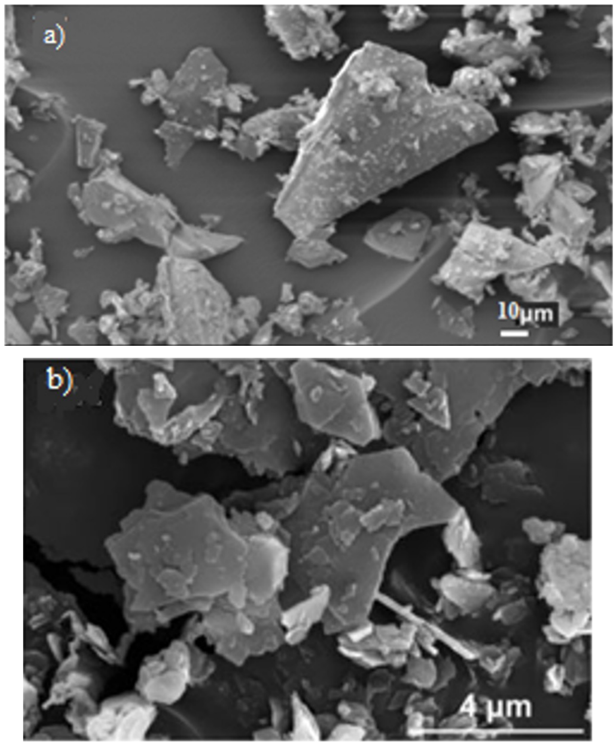

Figure 2. Microstructure of (a) milled glass (b) metakaolin.

The cement composites were mixed mechanically using a laboratory mortar mixer. The mixing time was 240 seconds. The mixed paste was poured into standard 40 × 40 × 160 mm moulds and cured for 24 h. After one day the specimens were disassembled and further cured in water at 20 ± 1.0 °C for 27 days.

The physical and mechanical characteristics of the cementitious composite were determined according to LST EN ISO 1927-6:2013. The density, ultrasonic pulse velocity, compressive strength and flexural strength of the cementitious composite were determined for the specimens cured for 28 days and after 56 days of ASR exposure.

The alkali-aggregate reaction testing of the cementitious composite specimens was carried out according to RILEM recommended test method AAR-2. The procedure of the RILEM AAR-2 test method is as follows:

the specimens (40 × 40 × 160 mm) cured in water at 80 °C are kept in 1 M NaOH solution at 80 °C for 14 days. After 14 days their expansion is determined, considering that 0.054 % is the safe limit of expansion. The test is then continued for up to 56 days. After 56 days, the safe limit of expansion of the specimens is 0.1 % according to ASTM C 441 test method. The length L_n of the specimens placed into 80 ºC 1 M NaOH solution was recorded after 14 and 56 test days ± 2 hours. The expansion was calculated from the Equation:

$$Expansion, \% = 100 \cdot \left(\frac{L_n - L_0}{l}\right) \quad (1)$$

Here L_0 is the length of the specimen before immersion into sodium hydroxide solution, mm; L_n is the length of the specimens after 14 and 56 test days ± 2 hours in 1 M NaOH solution at 80 ºC, mm; l is the distance between the insertions in the specimens, mm.

The microstructure of the materials was analysed with the scanning electron microscope SEM JEOL JSM-7600F. The qualitative analysis of the mineral composition of the cementitious composite was carried out using the X-ray diffractometer DRON-7 with Cu anticatode, Ni filter, anode voltage 30 kV, anode current 12 mA, detector step 0.02º. ICDD database was used for peak decoding.

Phase analysis of crystallising admixture was done by X-ray diffraction meter SmartLab (Rigaku) with a rotating Cu anode X-ray generator tube of 9 kW. X-ray diffraction patterns were recorded in the angular range 5 – 75° (2θ), detector step 0.02°, detector movement speed 1° per minute. The database of crystal structures PDF-4+ (2016) was used for the analysis. The microstructure of CA was inspected using SEM Helios NanoLab 650.

Table 2. Mixing proportion of cement composite specimens.

Composition designation	CEM I (%)	MS (%)	MK (%)	TS (%)	Sand (%)	Water (%)	W/B
C	26.9	0	0	0	60.6	12.4	0.46
TS5	26.9	0	0	3	57.6	12.4	0.46
TS10	26.9	0	0	6.1	54.5	12.4	0.46
TS15	26.9	0	0	9	51.6	12.4	0.46
TS20	26.9	0	0	12.1	48.5	12.4	0.46
TS25	26.9	0	0	15.1	45.5	12.4	0.46
TS30	26.9	0	0	18.2	42.4	12.4	0.46
MS5	25.6	1.3	0	0	60.6	12.4	0.46
MS10	24.3	2.7	0	0	60.6	12.4	0.46
MS15	22.9	4.0	0	0	60.6	12.4	0.46
MS20	21.6	5.4	0	0	60.6	12.4	0.46
MK5	25.6	0.0	1.3	0	60.6	12.4	0.46
MK10	24.3	0.0	2.7	0	60.6	12.4	0.46
MK15	22.9	0.0	4.0	0	60.6	12.4	0.46
MK20	21.6	0.0	5.4	0	60.6	12.4	0.46
TS25+MIX20	21.6	1.3	4.0	15.15	45.45	12.4	0.46

RESULTS AND DISCUSSION

Density, ultrasonic pulse velocity (UPV), flexural and compressive strengths of the specimens where sand was replaced by crushed glass were determined prior to the alkali-aggregate reaction testing. The results of the tests are given in Table 3. Physical and mechanical properties of the specimens were analysed and the optimum amount of crushed glass was selected to replace part of the sand, i.e., 25 %. The results given in Table 3 show that the strength and density of the specimens increased with the increase of crushed glass content in the mix up to 25 %. Further increasing of crushed glass content did not improve the mechanical properties and did not increase the density of the specimens.

Table 3. Physical and mechanical properties of the specimens containing crushed glass after 28 days of curing in water.

Batch of specimens	Density ($kg \cdot m^{-3}$)	UPV ($m \cdot s^{-1}$)	Flexural strength (MPa)	Compressive strength (MPa)
C	2151	4211	7.7	51.0
TS5	2160	4220	7.8	52.0
TS10	2165	4233	7.8	52.0
TS15	2170	4233	7.9	54.6
TS20	2174	4240	7.9	58
TS25	2175	4215	8.0	51.7
TS30	2170	4215	7.1	50.0

Figure 3 illustrates the relationship between the expansion of the cementitious composite and crushed glass content in the mix. After 14 days of testing, the expansion of the control specimens and of the specimens in which sand was replaced by crushed glass by weight of cement from 5 % to 30 % ranged from 0.06 % to 0.76 % and exceeded the pessimum limit of 0.054 %. After 56 days of testing, the expansion of the specimens with crushed glass varied between 0.15 % and 0.76 % and also exceeded the pessimum limit of 0.1 %. It can be concluded that the use of crushed glass to replace part of the sand in concrete mix causes ASR related degradation of cementitious composites.

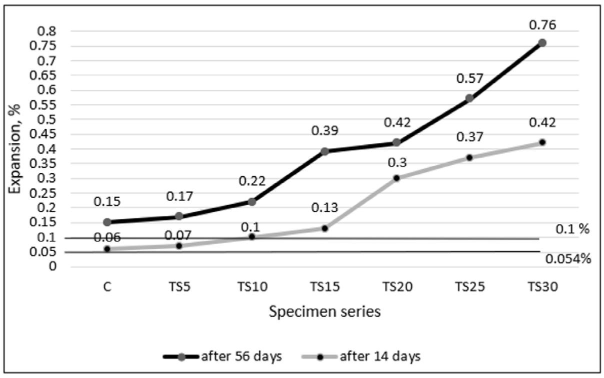

Figure 3. Expansion of cementitious composite specimens with crushed glass kept in 1 M NaOH solution at 80 °C for 14 and 56 days of testing as a function of the amount of crushed glass.

Figure 4 illustrates the surfaces of cementitious composite specimens containing crushed glass after 56 days of expansion testing at 80 °C in 1 M NaOH solution. Pictures of the tested bars show that the cracking on the surface of the specimens becomes more intensive with a higher content of crushed glass used to replace sand.

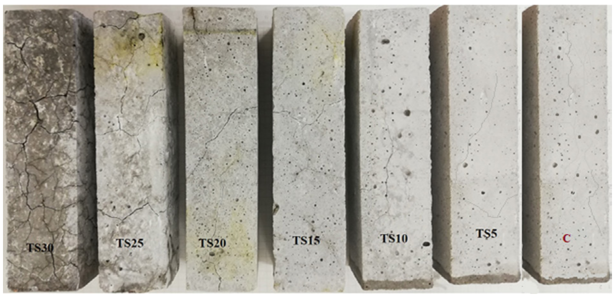

Figure 4. Surface of cementitious composite specimens containing crushed glass after 56 days of expansion testing in 1 M NaOH solution at 80 °C.

The effect of pozzolanic waste on cementitious composites was determined by further tests. First, the influence of the amount of milled glass used to replace part of the cement on the expansion of the cementitious composite was determined. The relationship between the expansion of cementitious composite specimens modified with milled glass and kept in 1 M NaOH solution at 80 °C for 14 and 56 test days and the amount of milled glass used to replace cement is shown in Figure 5.

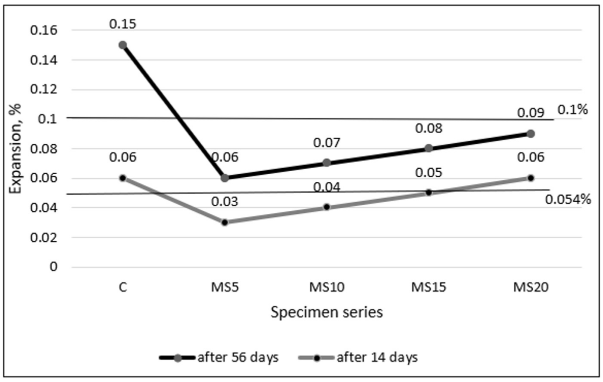

Figure 5. The relationship between the expansion of cementitious composite specimens with milled glass kept in 1 M NaOH solution at 80 ºC for 14 and 56 test days and milled glass content.

The expansion of cementitious composite specimens, in which milled glass replaced from 5 % to 20 % of cement, did not exceed the pessimum limit of 0.054 % after 14 days of testing. After 56 days of testing, the expansion of the specimens in which milled glass replaced from 5 % to 20 % of cement, did not exceed the pessimum limit of 0.1 %. The minimum expansion of 0.01 % after 14 days and 0.03 % after 56 days was observed in the specimens containing 5 % of milled glass by weight of cement. The expansion of the specimens increases with the increase of milled glass content. The same results were reported in the study of other authors [30]. The test results prove that the increase of milled glass in the mix significantly increases ASR caused expansion of the specimens after 7, 14 and 28 days.

Figure 6 shows the comparative results for density, ultrasonic pulse velocity, compressive strength, flexural strength for cementitious composite specimens cured for 28 days and tested from ASR caused expansion for 56 days. It was found that the control specimen was the most affected by the alkaline environment, with 2.4 % decrease in density from 2151 kg·m^{-3} to 2100 kg·m^{-3} due to faster ASR reaction, while the cementitious composite specimens in which 5 % of cement was replaced by milled glass were the least affected. The density of these specimens decreased by 1.9 % after the expansion tests (Figure 6a). The effectiveness of glass waste used to mitigate ASR-induced expansion greatly depends on the chemical composition of glass (especially the presence of K_2O) and the percentage of cement replacement with the additives. At the same time, calcium hydroxide consumption [31] is also strongly affected by these factors. The results of ASR-induced expansion tests are supported by the results of UPV tests. The greatest change in the structure after the expansion tests was recorded in control specimens. The UPV in these specimens reduced 11.0 % from 4211 m·s^{-1} to 3747 m·s^{-1}. The smallest change after the expansion tests was recorded in cementitious composite specimens where 5 % of the cement was replaced by milled glass. The UPV in these specimens reduced 7.6 % from 4245 m·s^{-1} to 3920 m·s^{-1}. The lower drop in UPV is explained by the smallest volume changes in the cementitious composite resulting in the smallest number and extent of microcracks (Figure 6b).

The expansion in alkaline environment affected the flexural strength that had decreased in all compositions of cementitious composite. The most significant decrease of 7.8 % was observed in control specimens. The replacement of cement with 5 % of milled glass resulted in the reduction of flexural strength by 4.9 % only, from 8.1 MPa to 7.7 MPa (Figure 6c).

Therefore, the cementitious composite specimens containing 5 % of milled waste glass experienced the least adverse effect caused by the alkaline environment. The lowest drop in density, ultrasonic pulse velocity, flexural and compressive strength values after ASR-induced expansion tests was recorded in the specimens of this composition.

Based on the results obtained in this study, 5 % of milled glass will be used to substitute cement in further studies carried out to develop a complex pozzolanic additive for cementitious composites.

The relationship between the expansion of cementitious composite modified with waste metakaolin

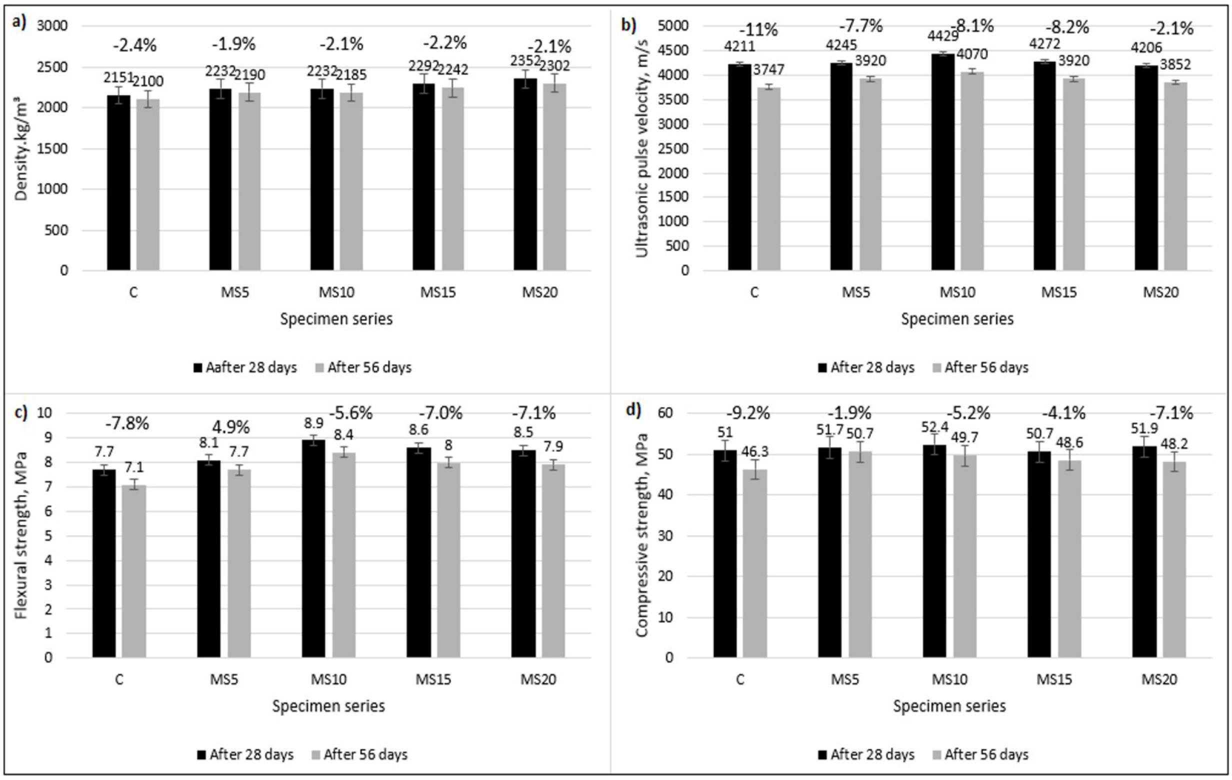

Figure 6. Variation of physical and mechanical properties in cementitious composite specimens with milled glass after 56 days of expansion tests at 80 °C in 1 M NaOH solution: a) density; b) ultrasonic pulse velocity; c) flexural strength; d) compressive strength.

The compressive strength of the cementitious composite also decreased after the exposure to alkaline environment. The most significant decrease of 9.2 % was observed in the compressive strength of control specimens. The same trend was observed by other authors [28,32]. The least drop in compressive strength of 1.9 % only was recorded in the specimens where 5 % of cement was replaced with milled glass (Figure 6d). Similar results were reported in other studies [33]. The authors found that the most effective mitigation of ASR-induced expansion and degradation of concrete was achieved by using up to 10 % of waste glass powder instead of cement.

and metakaolin content is shown in Figure 7. After 14 days of testing, the expansion of all specimens, except for control specimen, was within the permissible limit of 0.054 %. After 14 days of testing, the lowest expansion of 0.02 % was found in the specimens, in which cement was replaced by 15 % of waste metakaolin. The expansion of the specimens increased with the increase of metakaolin content in the cementitious composite mix. After 56 days of testing, the expansion of all specimens, except for control specimen, was also within the permissible limit of 0.1 %. The lowest expansion of 0.04 % after 56 days of testing was found in the specimens containing 15 % of metakaolin.

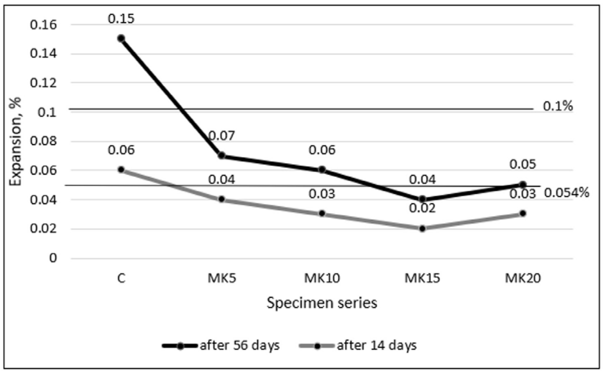

Figure 7. Relationship between the expansion of cementitious composite specimens with waste metakaolin kept in 1 M NaOH solution at 80 °C for 14 and 56 days and waste metakaolin content.

The same trend of increased expansion of the specimens with higher metakaolin content was observed. According to researchers [34-35], metakaolin reduces ASR-induced expansion of cementitious materials. Reduced levels of calcium in ASR products, which are associated with expansion, were identified in the presence of metakaolin. Researchers reported [36] that the optimal amount of metakaolin required to keep ASR-induced expansion < 0.04 % varies between 10 % and 15 %.

The greatest change in the structure after the expansion tests was recorded in control specimens. Their UPV decreased 11.0 % from 4211 $m \cdot s^{-1}$ to 3747 $m \cdot s^{-1}$. The smallest change after the expansion tests was recorded in the cementitious composite specimens where 15 % of cement was replaced by metakaolin. Their UPV decreased 8.2 % from 4275 $m \cdot s^{-1}$ to 3924 $m \cdot s^{-1}$ (Figure 8b).

The expansion caused by the alkaline environment affected the flexural strength of the cementitious composite, which decreased in all compositions. The most significant decrease in strength due to the change in structure was 7.8 % for the control specimens. The replacement of cement with 15 % of metakaolin reduced the flexural strength by 6.6 % from 8.2 MPa to 7.7 MPa (Figure 8c).

ASR-induced expansion reduces the compressive strength of cementitious composites. The most significant decrease of 9.2 % in compressive strength from 51.0 MPa to 46.3 MPa was observed in control specimens. Cement replacement with 15 % of metakaolin caused only 7.4 % reduction in compressive strength (Figure 8d). Authors reported [35] that the compressive strength of control specimens kept in alkaline solution for 28 days was 20 – 30 % lower than the strength of specimens kept under normal conditions. After 28 days of expansion testing, the compressive strength of specimens with metakaolin addition of 10 – 50 % by weight of cement was 10 – 2 % lower than the strength of specimens kept under normal conditions. This can be explained by improved solubility and reactivity of metakaolin in cementitious systems in alkaline environment.

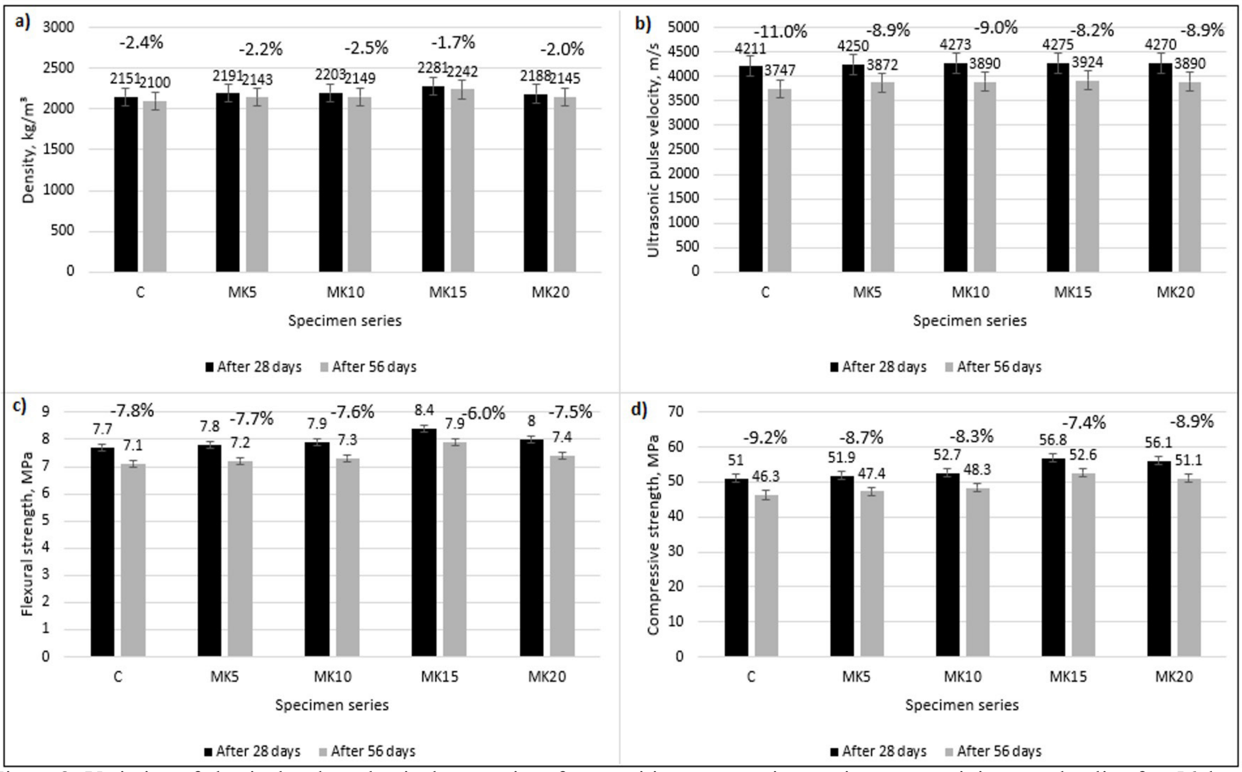

Figure 8. Variation of physical and mechanical properties of cementitious composite specimens containing metakaolin after 56 days of expansion tests at 80 °C in 1 M NaOH solution: a) density; b) ultrasonic pulse velocity; c) flexural strength; d) compressive strength.

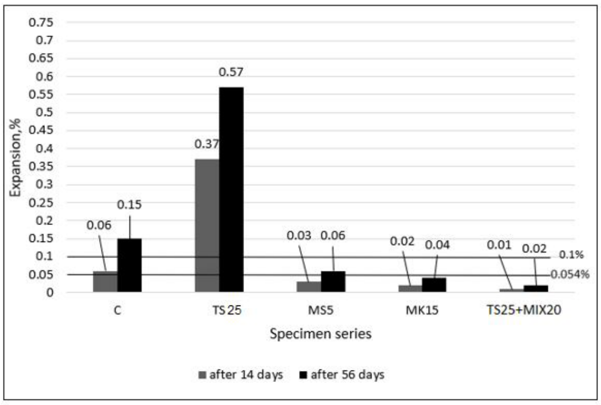

Figure 9. The limit values of cementitious composite specimens containing pozzolanic waste and crushed glass additives kept for 14 and 56 test days at 80 °C in 1 M NaOH solution.

The cementitious composite in which 15 % of the cement was replaced with metakaolin was the least adversely affected by the alkaline environment. This composite showed the lowest reduction in density, ultrasonic pulse velocity, flexural and compressive strength values after the ASR-induced expansion tests.

Based on the results obtained in this study, further studies will be carried out to develop a complex pozzolanic additive using 15 % waste metakaolin as a cement replacement in cement composite.

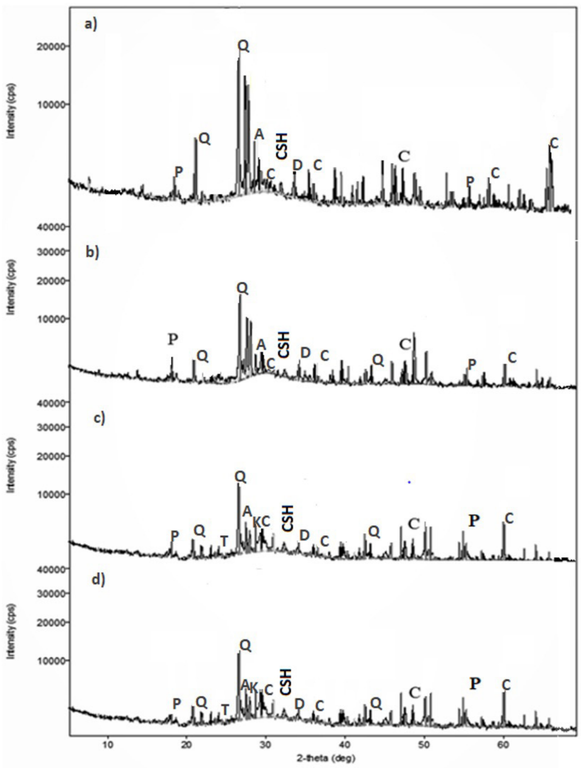

Figure 10. X-ray image of cement, the composite was maintained for 56 days in a 1 M NaOH solution at 80 ºC a) C; b) MS5; c) MK15; d) TS25+MIX20:
P - Portlandite; C - Calcite; Q - Quartz; D - Dolomite; T - Terranovaite; K - Katoite; A - Anorthite.

A comparison of the expansion of different cementitious composite specimens containing sand (C), crushed glass (TS), milled glass (MS5), metakaolin (MK15) and cementitious composite specimens containing crushed glass and a complex (milled glass and metakaolin) pozzolanic waste additive (TS25+MIX20) is shown in Figure 9. The expansion of the control specimens (C) after 14 days is 11 % above the pessimum limit of 0.054 % and after 56 test days the expansion is 0.15 %, i.e., 50 % above the pessimum limit of 0.1 %. After 14 days, the expansion of cementitious composite specimens in which 25 % of sand was replaced with crushed glass was 0.37 %, i.e., almost 7 times higher than the pessimum limit of 0.054 %. After 56 days of testing, the expansion of the test specimens was 0.57 %, i.e., 5.7 times higher than the pessimum limit of 0.1 %. These results show that crushed glass in cementitious composite significantly reduces the resistance to ASR-induced expansion and degradation of modified specimens compared to control specimens (C).

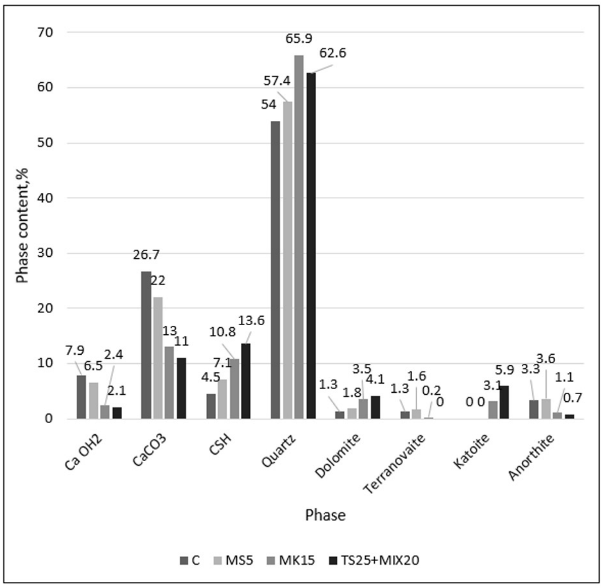

Figure 11. Phase content (%) in the composition after ASR test.

When 5 % of cement is replaced with crushed glass, the expansion of cementitious composite specimens is 0.03 % after 14 days of testing and 0.06 % after 56 days of testing, and thus below the pessimum limit of 0.054 %. The replacement of 15 % of cement with metakaolin results in 0.02 % and 0.04 % expansion of the cementitious composite specimens after 14 and 56 days respectively. As stated by the authors [37], the addition of 15.0 % of metakaolin was sufficient to compensate the ASR-induced expansion within the acceptable limits prescribed by the ASTM C1260 standard. Thus, cementitious composites with both milled glass and metakaolin are resistant to ASR-induced expansion and degradation, with 40 % expansion at 56 days being 60 % below the pessimum limit. The CaO/SiO_2 ratio in the specimen also decreases with the use of glass or metakaolin due to the decreased cement content. It is known that the expansion of the specimens decreases with a lower CaO/SiO_2 ratio in the system [38].

The use of a complex pozzolanic admixture consisting of 5 % of milled glass and 15 % of metakaolin in a cementitious composite and the replacement of 20 % of cement with this admixture as well as 25 % of the sand with crushed glass in the mix produces the expansion of modified specimens was within the permissible limit. The expansion of the specimens made of the above mix was the lowest among all composite specimens tested (Figure 9). The TS25+MIX20 specimens showed an expansion of 0.01 % after 14 days of testing and 0.02 % after 56 days test. The obtained results prove that the use of 5 % of milled glass in combination with 15 % of metakaolin can significantly reduce the expansion in the specimens where 25 % of sand is replaced with crushed glass, which has been shown to significantly increase the expansion of the specimens in the expansion tests (Figure 3). Thus, a significant result has been obtained showing that the developed composite TS25+MIX20 is resistant to ASR-induced degradation despite the use of 45 % of waste in the mix. According to the literature [28, 35, 39], the ternary combination of SCMs was more efficient and effective than the binary blend, which addressed not only the durability of concrete, the resistance to ASR, but also its mechanical characteristics.

X-ray diffraction analysis (Figure 10) were carried out to determine the effect of alkaline environment on the mineral changes in cementitious composite with pozzolanic waste additives after 56 test days. The changes in the properties of the cementitious composite after soaking in alkaline solution are caused by the transformation of cement hydration products in the alkaline environment. Cement hydration products, such as portlandite and CSH, were detected in all tested specimens kept in the alkaline solution for 56 days. Quartz, $CaCO_3$, dolomite, anorthite were also seen in the XRD curve of all specimens. Additional reaction products, such as Terranovaite (Ca-3.89; Na-4.43); (Al-12.30; Si-67.70; O-160) (H_2O)46.48) resulting from keeping the specimens in alkaline solution was found. XRD patterns showed the decreasing CaO/SiO_2 ratio. It was observed [40] that alkali retention in C-S-H gel increased by lowering the CaO/SiO_2 ratio when Si rich additives were used in the mix.

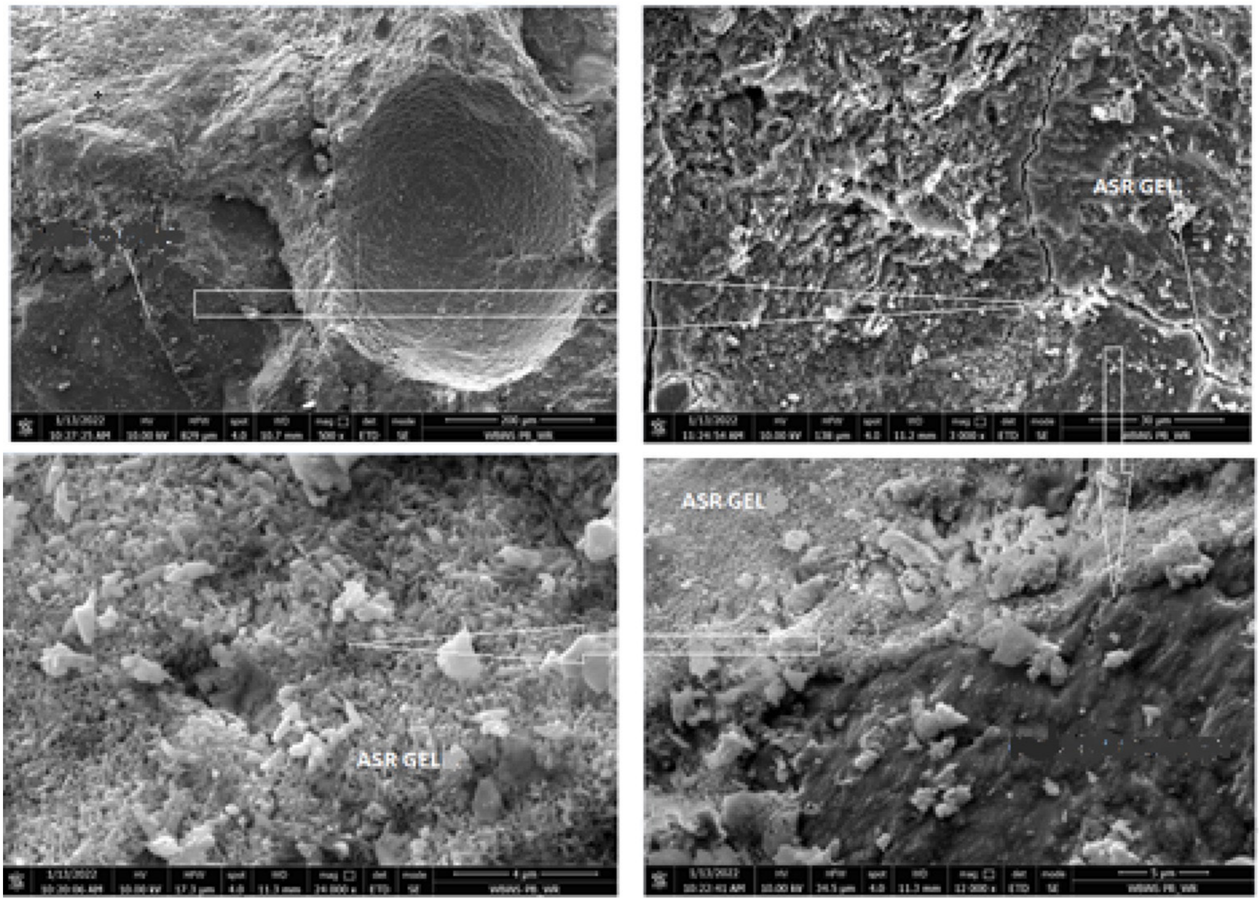

Figure 12. Microstructure of the cementitious composite control specimens retained for 56 test days at 80 °C in 1 M NaOH solution.

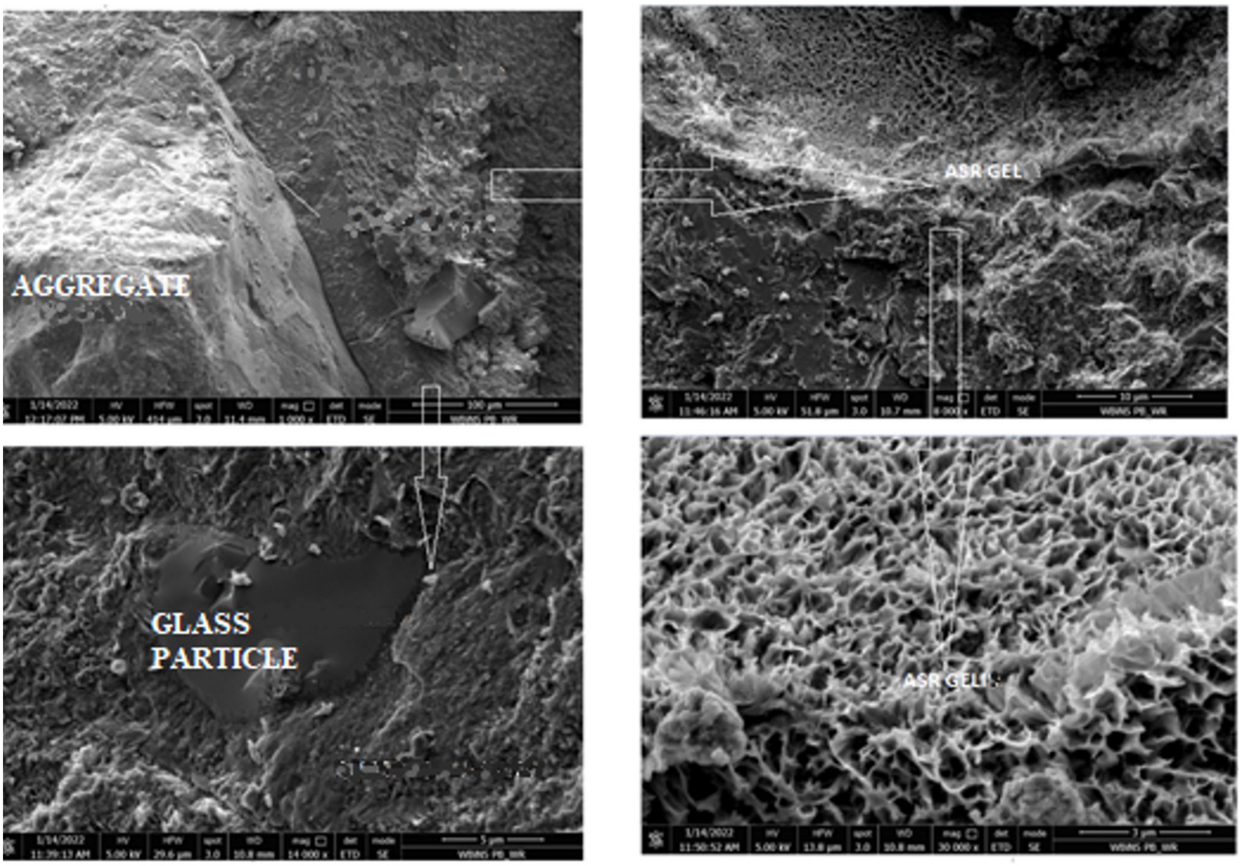

Figure 13. Microstructure of cementitious composite specimens with milled glass additive kept at 80 °C in 1 M NaOH solution for 56 test days.

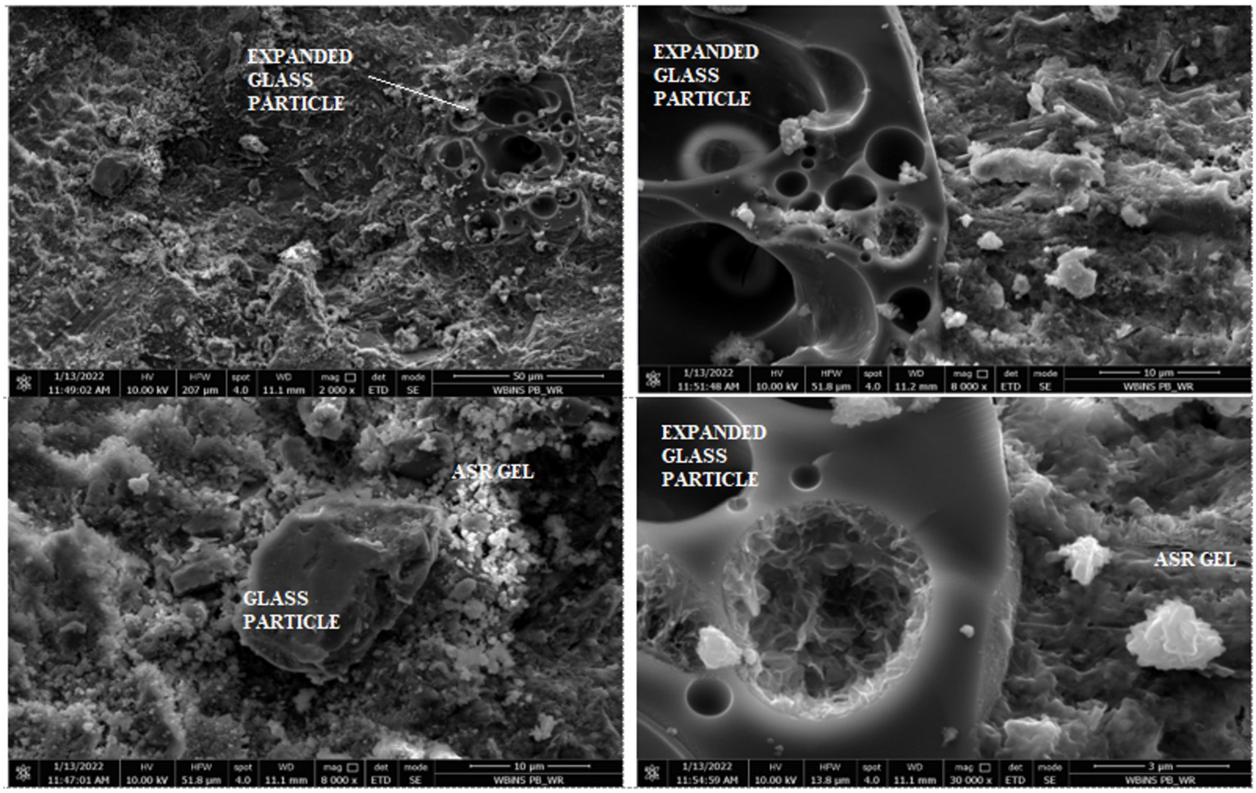

Figure 14. Microstructure of cementitious composite specimens with metakaolin additive kept at 80 °C in 1 M NaOH solution for 56 test days.

The percentage of portlandite in the specimens reduced as the amount of cement in the specimens decreases, respectively from 7.9 % to 2.1 %, when the replacement of cement with pozzolanic additives in the specimens reached 20 % (Figure 11). Lower portlandite content can reduce the ASR-induced expansion significantly by the consumption of high amorphous silica from the pore solution [18].

The presence of CSH was observed in all specimens [41]. Most of CSH (13.6 %) and additionally formed katoite ($Ca_3Al_2(SiO_4)_{0.64}(OH)_{9.44}$), the amount of which increased up to 5.9 %, were produced in the specimen TS25+MIX20, which contained both milled glass and waste metakaolin. It can happen as higher consumption of portlandite in the presence of the additives used in our specimens were reported by other authors [42-43]. It was proved by other researchers [44] that the presence of alumina in the composite (metakaolin in our case) accelerate C-S-H and C-A-S-H gel formation, which in turn improve the alkali binding capacity. In our tests the amount of katoite formed in the specimens M15 and TS25+MIX20 increased significantly. This is also confirmed by the fact that the content of the mineral terranovaite in the specimen M15 was only 0.2 %, while in the specimen TS25+MIX20 terranovaite was not identified at all.

$CaCO_3$ formation depends significantly on the amount of pozzolanic additives in the specimen. The amount of calcite in the composition was also affected by the amount of cement. It tends to decrease as less $Ca(OH)_2$ is produced in the specimens, allowing it to react with CO_2 from the atmosphere [45]. Besides, some increase in the dolomite content in the specimens with pozzolanic additive was observed.

In summary, a higher amount of pozzolanic waste decreases the amount of calcite and portlandite in the specimens. This indicates that calcium ions are involved in secondary cement hydration processes, resulting in the formation of more hydration products which densify, strengthen and protect the microstructure of the cement composite from ASR effects.

The radiographic analysis of the cementitious composite specimens after ASR expansion tests was complemented by microstructural studies. The microstructure was examined by electron microscopy. Figure 12 shows the SEM analysis of the control specimen. After the exposure of cementitious composite specimens without pozzolanic waste additives to the alkaline corrosive environment, ASR gel formed around the aggregate, which expanded and damaged the microstructure of the cementitious matrix. The microstructure of the cementitious composite

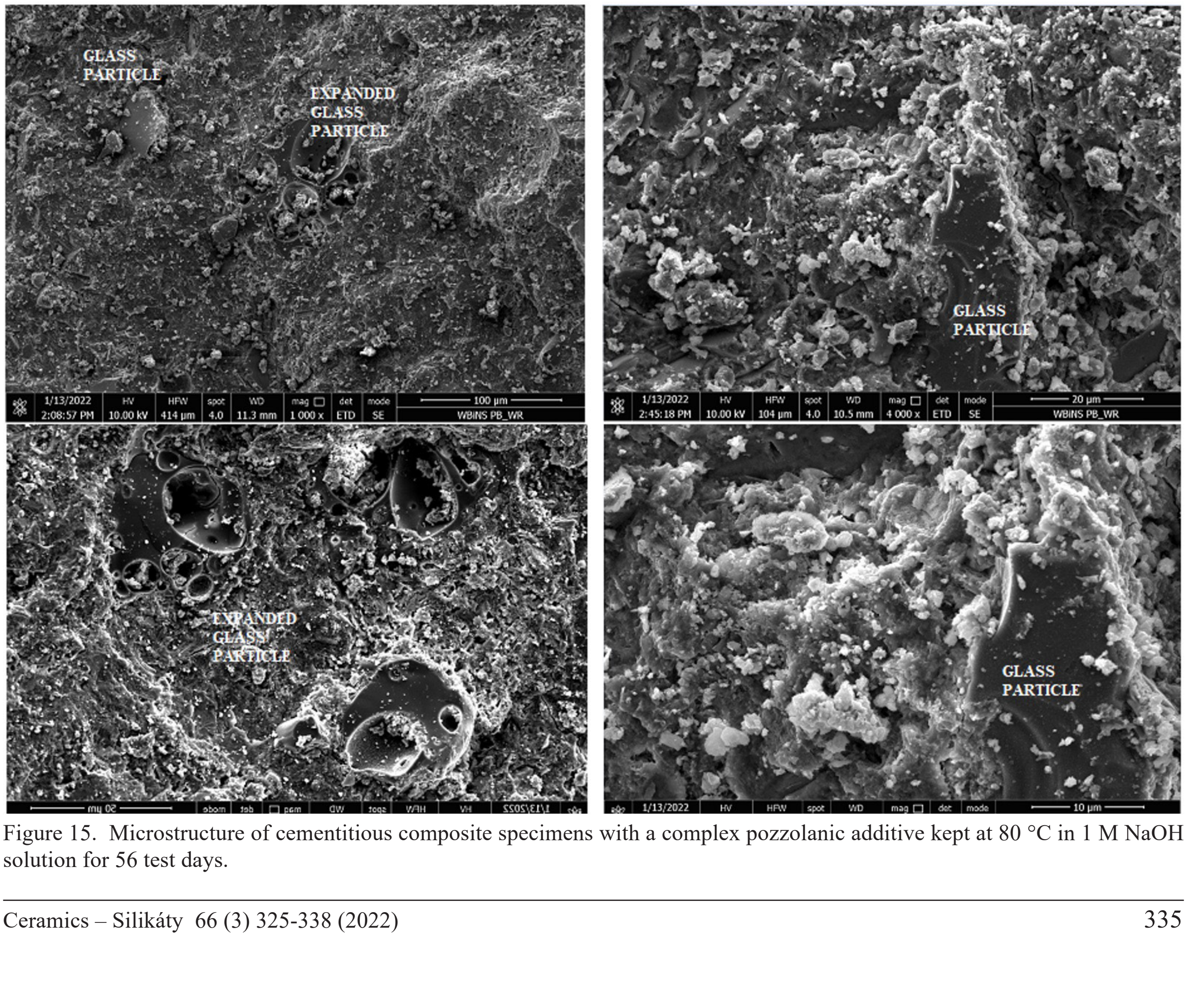

Figure 15. Microstructure of cementitious composite specimens with a complex pozzolanic additive kept at 80 °C in 1 M NaOH solution for 56 test days.

is damaged due to ASR-induced expansion and thus the physical and mechanical properties of the cementitious composite deteriorate.

Figure 13 shows a SEM image of the specimen containing 5 % of milled glass. The contact zones between the aggregates and the cementitious matrix and the formation of an ASR gel, which disrupts the microstructure of the cementitious composite, are seen in the image.

Figure 14 shows an SEM image of a cementitious composite with waste metakaolin additive. ASR gel is seen next to the aggregate particle. After the exposure to alkaline environment, the microstructure of the cementitious composite with metakaolin additive shows a much stronger contact zone between the aggregate and the cementitious matrix, with few, if any, gaps, compared to the specimens without pozzolanic waste. There is less damage to the cement matrix. The ASR gel content and distribution is lower than in the control specimens.

Figure 15 shows a SEM image of cementitious composite with a mixed pozzolanic additive. A particle of crushed glass aggregate and a dense cementitious matrix formed around it is seen in the image. The microstructure of the cementitious composite modified with 20 % of the mixed pozzolanic waste additive shows that the contact zone between the aggregate and the cementitious matrix is very strong, with no cracks or other deterioration of the matrix visible. This is typical of cementitious composite surfaces affected by ASR.

The specimens of this batch containing 25 % of crushed glass instead of sand and 20 % of the mixed pozzolanic waste additive consisting of 5 % milled glass and 15 % metakaolin are resistant to ASR-induced expansion and degradation.

The use of waste glass and metakaolin in the production of cementitious composites provides a solution to the problem of waste glass and metakaolin recycling and subsequently reduce the pollution of the environment. These factors make it possible to utilise large quantities of glass and metakaolin waste in concrete manufacturing as substitutes for cement and sand. The new formulation of cementitious composite can be used for the production of ASR resistant cementitious composites with low cement content.

CONCLUSIONS

The tests showed that the expansion of cementitious composite control specimens and the specimens where sand was replaced with 5 % to 30 % crushed glass exceeds the limit of 0.054 % after 14 days of testing and varied between 0.06 % and 0.76 %, depending on the amount of crushed glass. Correspondingly, after 56 days of testing, the expansion of the specimens exceeds the limit of 0.1 % and varied between 0.15 % and 0.76 %. It is evident that the use of crushed glass as a sand substitute in cementitious composites increases the pessimum ASR-induced expansion limit by a factor of 7.

The expansion of cementitious composite specimens with part of the cement replaced by milled glass (between 5 % and 20 %) does not exceed the pessimum limit of 0.054 % after 14 and 56 days of testing. The minimum expansion of the specimens containing 5 % of milled glass was 0.01 % and 0.03 % respectively. The expansion of the specimens increases with the increase of milled glass content in the mix.

Compared to the control specimens, the expansion of all cementitious composite specimens modified with waste metakaolin additive that replaces from 5 % to 20 % of cement is within the pessimum limits of 0.054 % and 0.1 % after 14 and 56 days of testing respectively. The expansion of the specimens increases with further increase of metakaolin content. The lowest expansion of 0.02 % and 0.04 % after 14 and 56 test days was found in the specimens, in which 15 % of cement was replaced with metakaolin.

The use of a complex pozzolanic addition consisting of 5 % MS and 15 % FC to replace 20 % of cement in cementitious composite mix and also the replacement of 25 % of the sand by crushed glass results in the expansion of the specimens within the permissible limits at 14 and 56 days of testing. This expansion is also the lowest among all cementitious composites with metakaolin and with crushed sand tested. The expansion of cementitious composite specimens containing a complex pozzolanic additive is 0.01 % and 0.02 % after 14 and 56 days of testing. The cementitious composite of this composition is resistant to ASR-induced degradation and has a high waste content of 45 %.

XRD and microstructural analyses have shown that the reduction in expansion is due to the higher content of hydration products such as CSH and katoite, as well as to the denser, intact contact zone between the aggregate and the cementitious matrix in modified specimens compared to the specimens without pozzolanic waste. The microstructure of the cementitious composite modified with 20 % of mixed pozzolanic waste additive does not show any cracks in the contact zone between the aggregate and the cementitious matrix or any other degradation typical of ASR affected surfaces of cementitious composites. Such formation of the microstructure has a positive effect on the physical and mechanical properties of the cementitious composite and its high resistance to alkali attack.

The use of waste glass and metakaolin in the production of cementitious composites provides a solution to the problem of waste glass and metakaolin recycling and subsequently reduce the pollution of the environment. These factors make it possible to utilise large quantities of glass and metakaolin waste in concrete manufacturing as substitutes for cement and sand. The new formulation of cementitious composite can be used for the production of ASR resistant cementitious composites with low cement content.

REFERENCES

1. Halbiniak J., Major M. (2019). The Use of Waste Glass for Cement Production. In: *IOP Conference Series: Materials Science and Engineering* (Vol. 585, No. 1, p. 012008). IOP Publishing. doi:10.1088/1757-899X/585/1/012008
2. Guignone G. C., Vieira G. L., Zulcão R., Degen M. K., Mittri S., Teles C. R. (2020): Performance of concrete with the incorporation of waste from the process of stoning and polishing of glass as partial replacement of cement. *Revista IBRACON de Estruturas e Materiais, 13*, 613-627. doi:10.1590/S1983-41952020000300011
3. Guo S., Dai Q., Sun X., Xiao X., Si R., Wang J. (2018): Reduced alkali-silica reaction damage in recycled glass mortar samples with supplementary cementitious materials. *Journal of Cleaner Production, 172*, 3621-3633. doi:10.1016/j.jclepro.2017.11.119
4. Wang Y., Cao Y., Zhang P., Ma Y. (2020): Effective utilization of waste glass as cementitious powder and construction sand in mortar. *Materials, 13*(3), 707. doi:10.3390/ma13030707
5. Paul S. C., Šavija B., Babafemi A. J. (2018): A comprehensive review on mechanical and durability properties of cement-based materials containing waste recycled glass. *Journal of Cleaner Production, 198*, 891-906. doi: 10.1016/j.jclepro.2018.07.095
6. Thankam G. L., Thurvas Renganathan N. (2020):Ideal supplementary cementing material – Metakaolin: A review. *International Review of Applied Sciences and Engineering IRASE, 11*(1), 58-65. doi:10.1556/1848.2020.00008
7. Chander S. V., Ramakrishnan K.,Muthu D. (2018): Experimental Study on Mechanical Properties on Ternary Blend of Concrete. *International Journal of Engineering & Technology, 7*, 910-914. doi:10.14419/ijet.v7i3.12.16559
8. Prakash G., Suman S. K., Kumar M. (2021): Influence of Metakaolin Content on the Properties of Pavement Quality Concrete. *Trends in Transport Engineering and Applications,* 8(2), 8–20.
9. Liu S., Wang S., Tang W., Hu N., Wei J. (2015): Inhibitory effect of waste glass powder on ASR expansion induced by waste glass aggregate. *Materials, 8*(10), 6849–6862. doi:10.3390/ma8105344
10. Tognonvi M.T., Tagnit-Hamou A., Konan L.K., Zidol A., N'Cho W.C. (2020): Reactivity of Recycled Glass Powder in a Cementitious Medium. *New Journal of Glass and Ceramics, 10*, 29-44. doi:10.4236/njgc.2020.103003
11. Ferraris C.F. (1995). *Alkali-Silica reaction and high-performance concrete*. NISTIR 5742. Pp: 1-19. doi:10.6028/NIST.IR.5742
12. Bocullo V., Grinys A. (2013): Betono su aktyviaisiais mineraliniais priedais šarminės korozijos tyrimas. In: *16th Conference for Junior Researchers „Science – Future of Lithuania"*. Vol. 16., 1-8.
13. Jongprateep O., Jaroonvechatam N., Meesak T., Sujjavanich S. (2018): Effects of glass and limestone aggregates and aluminium on porosity, expansion, and strength of mortar bars. *Materials Today:Proceedings, 5*, 93069311, doi:10.1016/j.matpr.2017.10.104
14. Ke G., Li W., Li R. et al. (2018): Mitigation Effect of Waste Glass Powders on Alkali–Silica Reaction (ASR). Expansion in Cementitious Composite. *International Journal of Concrete Structures and Materials, 12*, 67 doi:10.1186/s40069-018-0299-7
15. Disfani M.M., Arulrajah A., Bo M.W. (2012): Sivakugan N.,Environmental risks of using recycled crushed glass in road applications. *Journal of Cleaner Production, 20*, 170-179, doi:10.1016/j.jclepro.2011.07.020.
16. Nurhayat D., Arin Y., Andic C. (2011): Utilization of waste glass as sand replacement in cement mortar. Indian Journal of Engineering and Materials Sciences, 18, 303-308.
17. Sims I., Nixon P. (2003): RILEM recommended test method AAR1: Detection of potential alkali-reactivity of aggregates—Petrographic method. *Materials and Structures, 36*, 480-496. Doi: 10.1007/BF02481528.
18. Saha A.K., Khan M.N.N., Sarker P.K., Shaikh F.A. (2018): Pramanik A. The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials, 171*, 743-758. doi:10.1016/j.conbuildmat.2018.03.183
19. Shayan A., Xu A. (2004): Value-added utilisation of waste glass in concrete. *Cement and Concrete Research, 34*, 81-89. doi: 10.1016/S0008-8846(03)00251-5
20. Idir R., Cyr M., Tagnit-Hamou A. (2010): Use of waste glass in cement-based materials. *Déchets sciences et techniques, 57*, 1-10.
21. Mien T. V. ., Nawa T., Stitmannaithum B., Tuan Anh N. D. (2022): Alkali silica reaction of recycled glass aggregate mortar using fly ash under steam curing. *Asean Engineering Journal, 12*(1), 149-155. doi:10.11113/aej.v12.17303
22. Serpa D., Santos Silva A., Brito J., Pontes J., Soares D. (2013): ASR of mortars containing glass. *Construction and Building Materials, 7*, 489-495. Doi: 10.1016/j.conbuildmat.2013.05.058
23. Zhang J., Liu G., Chen B., Song D., Qi J., Liu X. (2014): Analysis of CO2 Emission for the Cement Manufacturing with Alternative Raw Materials: A LCA-based Framework. *Energy Procedia, 61*, 2541-2545. doi: 10.1016/j.egypro.2014.12.041
24. Dinakar P., Sahoo P.K. Sriram G. (2013): Effect of Metakaolin Content on the Properties of High Strength Concrete. *International Journal of Concrete Structures and Materials, 7*, 215–223. doi: 10.1007/s40069-013-0045-0
25. Bheel N., Abbasi S.A., Awoyera P., Oladimeji B. Sohu S., Rondon C., Echeverría A.M. (2020): Fresh and Hardened Properties of Concrete Incorporating Binary Blend of Metakaolin and Ground Granulated Blast Furnace Slag as Supplementary Cementitious Material. *Advances in Civil Engineering, 2020*, 8851030. doi: 10.1155/2020/8851030
26. Liaudat J., Carol I., López C.M. (2020): Model for alkali-silica reaction expansions in concrete using zero-thickness chemo-mechanical interface elements. *International Journal of Solids and Structures, 207*, 145-177. doi:10.1016/j.ijsolstr.2020.09.019
27. Huang D., Sun P., Gao P., Liu G., Wang Y., Chen X. (2021): Study on the Effect and Mechanism of Alkali–Silica Reaction Expansion in Glass Concrete. *Sustainability, 13*(19), 10618. doi:10.3390/ su131910618
28. Fanijo O.E., Kassem E., Ibrahim A. (2021): ASR mitigation using binary and ternary blends with waste glass powder.

Construction and Building Materials, 280, 122425. doi: 10.1016/j.conbuildmat.2021.122425

29. Ouldkhaoua Y., Benabed B., Abousnina R., Kadri E.,H., Khatib J. (2020): Effect of using metakaolin as supplementary cementitious material and recycled CRT funnel glass as fine aggregate on the durability of green self-compacting concrete. *Construction and Building Materials, 235*, 117802. doi: 10.1016/j.conbuildmat.2019.117802
30. He P., Zhang B., Lu J. X., Poon C. S. (2020): ASR expansion of alkali-activated cement glass aggregate mortars. *Construction and Building Materials, 261*, 119925. doi: 10.1016/j.conbuildmat.2020.119925
31. Zheng K. (2016): Pozzolanic reaction of glass powder and its role in controlling alkali–silica reaction. *Cement and Concrete Composites, 67*, 30-38. doi: 10.1016/j.cemconcomp.2015.12.008
32. Leemann A., Le Saout G., Winnefeld F., Rentsch D., Lothenbach B. (2011): Alkali–Silica Reaction: the Influence of Calcium on Silica Dissolution and the Formation of Reaction Products. *Journal of the American Ceramic Society, 94*, 1243-1249. doi: 10.1111/j.1551-2916.2010.04202.x
33. Cai Y., Xuan D., Poon C. S. (2019): Effects of nano-SiO2 and glass powder on mitigating alkali-silica reaction of cement glass mortars. *Construction and Building Materials, 201*, 295-302. doi: 10.1016/j.conbuildmat.2018.12.186
34. Wei J., Gencturk B., Jain A., Hanifehzadeh M. (2019): Mitigating alkali-silica reaction induced concrete degradation through cement substitution by metakaolin and bentonite. *Applied Clay Science, 182*, 105257. doi: 10.1016/j.clay.2019.105257
35. Chappex T., Scrivener K. L. (2012): The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction. *Cement and Concrete Research, 42*, 1645-1649. doi: 10.1016/j.cemconres.2012.09.009
36. Ramlochan T., Thomas M., Gruber K. (2000): The effect of metakaolin on alkali–silica reaction in concrete. *Cement and Concrete Research, 30*, 339-344. doi: 10.1016/S0008-8846(99)00261-6
37. Cota F. P., Melo C. C. D., Panzera T. H., Araújo A., G., Borges P. H. R., Scarpa F. (2015): Mechanical properties and ASR evaluation of concrete tiles with waste glass aggregate. *Sustainable Cities and Society, 16*, 49-56. doi: 10.1016/j.scs.2015.02.005.
38. Saha A. K., Khan M.N.N., Sarker P. K., Shaikh F. A., Pramanik A. (2018): The ASR mechanism of reactive aggregates in concrete and its mitigation by fly ash: A critical review. *Construction and Building Materials, 171*, 743-758. doi: 10.1016/j.conbuildmat.2018.03.183
39. Ramlochan T., Thomas M., Gruber K. A. (2000):The effect of metakaolin on alkali–silica reaction in concrete. *Cement and Concrete Research, 30*, 339-344. doi: 10.1016/S0008-8846(99)00261-6.
40. Bhatty M.S.Y., Greening N.R. (1978): Interaction of alkalies with hydrating and hydrated calcium silicates, in: *Proceedings of the Fourth International Conference on the Effects of Alkalis in Cement and Concrete*. Purdue, pp. 87–112.
41. Xupeng C., Zhuowen S., Jianyong P. (2021): Study on Metakaolin Impact on Concrete Performance of Resisting Complex Ions Corrosion. *Frontiers in Materials, 8*, 788079. doi: 10.3389/fmats.2021.788079
42. Shehata M.H., Thomas M.D. (2002): Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali–silica reaction in concrete. *Cement and Concrete Research, 32*, 341-349. doi: 10.1016/S0008-8846(01)00680-9
43. Aquino W., Lange D.A., Olek J. (2001): The influence of metakaolin and silica fume on the chemistry of alkali–silica reaction products. *Cement and Concrete Composites, 23*, 485-493. doi: 10.1016/S0958-9465(00)00096-2
44. Hong S. Y., Glasser F. P. (1999): Alkali binding in cement pastes Part I. The C-S-H phase. *Cement and Concrete Research, 29*, 1893-1903. doi: 10.1016/S0008-8846(99)00187-8
45. Shih S. M., Ho C. U. S., Song Y. S., Lin J. P. (1999): Kinetics of the reaction of Ca (OH) 2 with CO_2 at low temperature. *Industrial & Engineering Chemistry Research, 38*(4), 1316-1322. doi: 10.1021/ie980508z