

Article

The Impact of Plasticizers on the Nature of the Alkali-Silicate Corrosion in Cement Composites

Andrey P. Pustovgar ¹, Yury R. Krivoborodov ², Aleksey O. Adamtsevich ^{1,*}, Aurika A. Elenova ¹, Kseniya A. Butenko ¹, Dmitrii V. Kramerov ¹ and Anton M. Bugaev ¹

¹ Scientific Research Institute of Construction Materials and Technologies, Moscow State University of Civil Engineering, Yaroslavskoe Shosse, 26, Moscow 129337, Russia; pustovgarap@mgsu.ru (A.P.); elenevaa@mgsu.ru (A.A.E.); butenkoka@mgsu.ru (K.A.B.); kramerovdv@mgsu.ru (D.V.K.); bugaevam@mgsu.ru (A.M.B.)

² Department of Chemical Technology of Composite and Binding Materials, Mendeleev University of Chemical Technology, Moscow 125047, Russia; ykriv@rambler.ru

* Correspondence: adamtsevichao@mgsu.ru

Abstract: This research work attempts to reveal the mechanism of alkali corrosion in cement composites in the presence of plasticizers based on polycarboxylates (PCE), naphtha-lene-formaldehydes (SPNF), and lignosulfonates by maintaining a high pH of the liquid phase and additionally containing monovalent alkali earth metals in cement stone, as well as stopping this process by introducing an active mineral additive. ASR is studied by changing the relative strain with time according to ASTM C-1260. Deformation changes were confirmed by SEM and RFA studies of hydration products and ASR in the microstructure. Separate use of PCE plasticizers in the cement composition increases deformation by 50% to the 56th day; the use of SPNF increases deformation by 10% compared with the additive-free composition. The use of PLS reduces the relative deformation by 25%. The introduction of silica fume into cementitious composites containing plasticizers actually stops ASR only for a short time. A reduction in deformation during MC use together with plasticizer based on naphthalene sulfonate and polycarboxylate occurs only when the dosage of MS is increased to 20–30%; at a lower dosage, the effect is negative, which also affects the phase composition of the composites. The introduction of MC increases the value of the relative deformation compared with plasticizer compositions based only on PLS. SEM studies have detected microcracks and dense fine-crystalline silicate gel, which cause deformation changes in cement composite samples. Research has shown that concrete modified with SPNF and PCE at the maximum dosage of MC (30%) has minimal deformation rates and can be used to select optimal concrete compositions. The results of this study could help to minimize risks, prevent unacceptable expansion, and ensure the high quality of concrete and concrete products during their use as part of various nature-modifying additives.



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1. Introduction

In the world practice of reinforced concrete application in the 1940s, cases of concrete corrosion destruction in structures in the absence of an externally aggressive environment were established, and later this phenomenon acquired the name of alkali-silica reaction (ASR) [1]. During the same period, the American Society of Civil Engineers (ASCE) published Stanton's article [2], which was the first comprehensive research work on ASR and contained confirmation that a destructive reaction would only occur if Portland cement contained a sufficient number of alkalis in the cement structure composite and reactive silica in the aggregate.

A high alkali content leads to an increase in the pH of the concrete pore solution. The high pH index is primarily due to the supply of alkali from Portland cement [3–8]. Other sources of alkali are concrete additives containing alkali, in particular superplasticizers.

The entry of alkalis is also possible from aggregates, as well as deicing reagents in contact with concrete structures [9–15].

One of the effective ways to combat the alkali-silicate reaction between the silicon oxides of the aggregate and the alkalis in the cement composite is through the use of active mineral additives such as microsilica, fly ash, and ground granulated slag. Such additives actively bind portlandite $\text{Ca}(\text{OH})_2$, which is intensively formed during the hydration of cement grains [16–21]. However, some studies have shown that the use of certain mineral supplements does not prevent ASR but rather contributes to the occurrence of this reaction [22–27].

As it is known, the use of finely ground mineral additives in concrete increases water demand, and the introduction of superplasticizers into the concrete mixture enables to reduce the amount of mixing water by 10–30%, depending on the type of superplasticizer, while maintaining the required mobility of the concrete mixture [28–30].

In the sources [31–33], it is noted that polycarboxylate superplasticizers contain oxides of the alkaline earth metals potassium and/or sodium, the presence of which can lead to increased alkalinity of the pore fluid and the likelihood of the alkali-silicate reaction. Typically, the alkali content in superplasticizers based on polycarboxylates in terms of Na_2O equivalent is in the range of 0.1 to 1%; those based on naphthalene, melamine, or lignin are in the range of 2 to 6% [34–36]. Even though the dosage of plasticizers in concrete production is in a low range, their effect on the process of alkali-silicate expansion cannot be completely excluded.

Currently, in several studies about the influence of superplasticizers on the course of ASR, it has been shown that the introduction of superplasticizers into the concrete mixture can lead to alkaline expansion, as determined by the method of testing concrete samples in the NaOH solution according to GOST 8269.0-97 or ASTM C 227 [37]. It should be noted that in this study, an unambiguous interpretation of the results is difficult since low-alkali cement was used as a binder and the alkali content in the cement was increased to 1.0% by adding NaOH [38].

Having adopted/assumed the ASTM C-1260 standard [39,40] as a test method, the study [40] showed that by adding a superplasticizer to compositions with high alkaline cement, an increase in expansion was recorded, and a decrease in expansion was recorded in mixtures made with low-alkali cement. In the method used, the solution samples were stored in a 1 N NaOH solution that affects the composition of the pore solution and therefore reduces or masks the effect of adding plasticizer.

For the above reasons, for a more thorough study of the alkali-silicate reaction with modifying additives, it was decided to consider the impact of superplasticizing additives based on polycarboxylates, naphthalene-formaldehydes, lignosulfonates, and the mineral additive microsilica.

The purpose of this study was to assess the effect of superplasticizers of different natures on the likelihood of internal alkaline corrosion, which can lead to a decrease in the durability of concrete and reinforced concrete structures.

This research work attempts to reveal the mechanism of alkali corrosion in cement composites in the presence of plasticizers based on polycarboxylates, naphthalene-formaldehydes, and lignosulfonates by maintaining a high pH of the liquid phase and additionally containing monovalent alkali earth metals in cement stone, as well as stopping this process by introducing an active mineral additive.

2. Materials and Methods

The relative deformations of fine-grained concrete samples with a dosage of superplasticizers of 0.5% were measured using the accelerated ASTM C-1260 method [29], and the structure of cement composites at design age was studied.

For the research work the most used in Russia materials for the concrete mixtures production were used:

- Portland cement CEM I 52,5H GOST 31108-2020 (LLC « Heidelbergcement Rus »), R₂ = 28.8 MPa, R₂₈ = 62.9 MIIa, normal consistency = 30.4%, beginning of setting—154 min.; uniform change in volume (expansion)—0.1%; C3S = 66.9%; C2S = 12.8%; C3A = 7%; C4AF = 13.2%; SO₃ = 3.0%, grinding intensifier—0.02%;
- Plasticizers based on lignosulfonates (PLS) «LSTM» production LLC «POLIPLAST», Russia, Novomoskovsk; ρ_{bulk} = 468 g/dm³, loss on ignition—1–2%; pH 20% solution at 200 °C—7 ± 1;
- Superplasticizers based on naphthalene formaldehyde (SPNF) «SP-1» production LLC «POLIPLAST», Russia, Novomoskovsk; ρ_{bulk} = 585 g/dm³, loss on ignition—1–2%; pH 20% solution at 200 °C—8 ± 1;
- Superplasticizers based on polycarboxylate esters (PCE) «Melflux 2651» production of the concern BASF, Germany) ρ_{bulk} = 456 g/dm³, loss on ignition—1.5–2%; pH 20% solution at 200 °C—7.5 ± 0.5;
- Microsilica MKU-85 (MC), according to GOST R 58894-2020,
- Polifraction sand according to GOST 6139-2020 production LLC «Polyquartz». The total balance on the sieves is: 2.00 mm—0%; 1.6 mm—6.8%; 1.00 mm—34.1%; 0.5 mm—66.5%; 0.16 mm—86.3%; 0.08 mm—99.7%.

Additives were introduced together with mixing water for uniform distribution throughout the volume of the concrete mixture.

To carry out the test, sample beams with dimensions of 25 × 25 × 254 mm (Figure 1) were made from a fine-grained concrete mixture consisting of cement and fine aggregate in a ratio of 1:2.25 by weight. To establish the general patterns of the impact of plasticizers and active mineral additives in the form of microsilica on the properties and structure of concrete, plasticizer additives were dosed in an amount of 0.5% by weight of cement, microsilica in an amount of 10%, 20%, or 30% by weight of cement, and part of the sand that had passed through a 0.16 mm sieve was replaced.

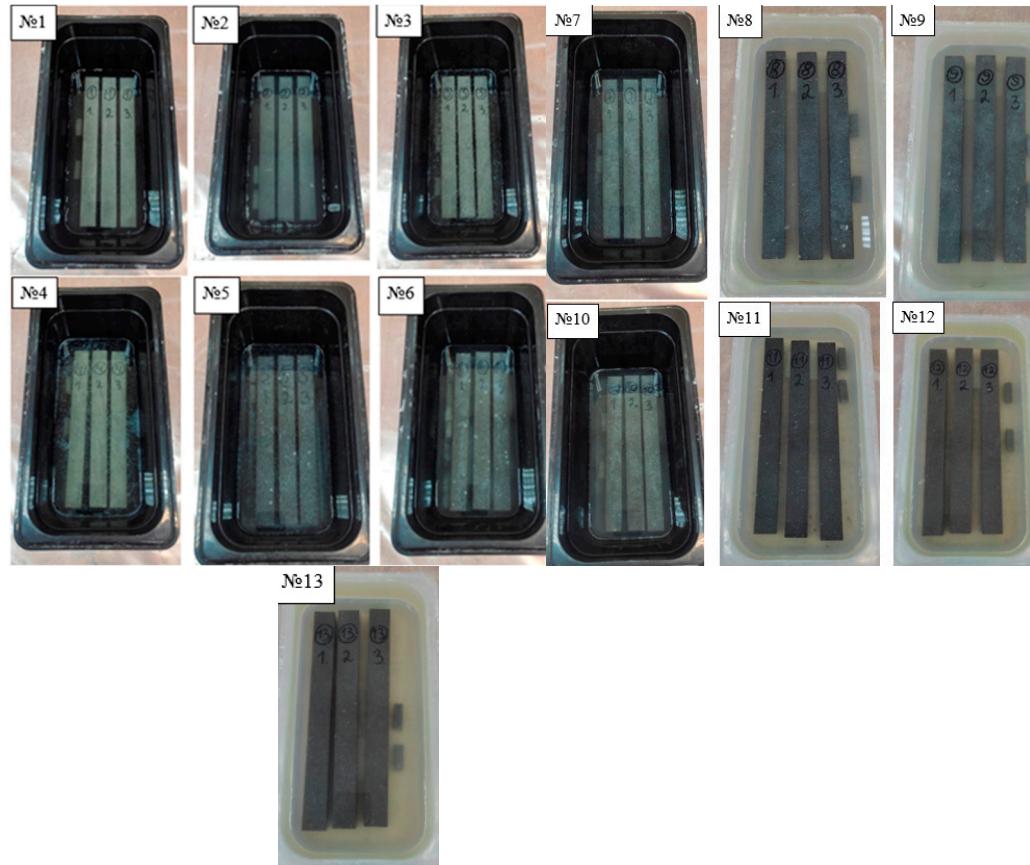


Figure 1. Storage of 25 × 25 × 254 mm samples before and between tests.

The water-cement (W/C) ratio was selected according to the spread of the cone (SC) after shaking the concrete mixture 15 times at a constant frequency of one beat per second. The cone spread for all compositions was assumed to be the same and equal to 140 ± 5 mm.

Tests to determine the relative deformations of concrete samples were carried out according to the accelerated ASTM C1260 method. A rapid test is carried out by immersing samples of concrete beams aged 48 h in a 1 mol NaOH solution at a temperature of $+80^\circ\text{C}$ (Figure 1). The relative deformations of the beam samples were recorded daily up to 14 days, and then measurements were carried out at intervals of 7 days.

The study of the physico-chemical properties and microstructure of concrete was carried out by powder X-ray diffraction using an ARL X'tra X-ray diffractometer and scanning electron microscopy on an FEI Quanta 200 scanning electron microscope with an Apollo 40 chemical analysis attachment (EDAX). Physicochemical studies were carried out when the samples were 7 and 56 days old.

3. Tests Results

To confirm the working hypothesis, three double experiments were planned and carried out. The responses were assigned to the W/C ratio at the same mobility, relative deformation from 2 to 56 days, phase composition, and local microanalysis of the structure at 7, 28, and 56 days. The experiment planning matrix is presented in Table 1.

Table 1. Matrix of the experiment with the obtained characteristics of the W/C ratio at $\text{PK} = 140 \pm 5$ mm.

No of the Composition	Name	Microsilica Content (MC)	Grams in One Mix			% of m(cem) Dry			W/C
			Portladcement	Sand	MC	PCE	SPNF-1	PLS	
1	Contr.	0% MC	600	1350	-	-	-	-	0.55
2	PCE		600	1350	-	0.5	-	-	0.23
3	SPNF-1		600	1350	-	-	0.5	-	0.34
4	PLS		600	1350	-	-	-	0.5	0.35
5	10%MC + PCE	10% MC from m(cem)	600	1290	60	0.5	-	-	0.28
6	10%MC + SPNF-1		600	1290	60	-	0.5	-	0.36
7	10%MC+ PLS		600	1290	60	-	-	0.5	0.38
8	20%MC + PCE		600	1230	120	0.5	-	-	0.35
9	20%MC + SPNF-1	20% MC from m(cem)	600	1230	120	-	0.5	-	0.43
10	20%MC + PLS		600	1230	120	-	-	0.5	0.43
11	30%MC + PCE		600	1170	180	0.5	-	-	0.45
12	30%MC + SPNF-1		600	1170	180	-	0.5	-	0.53
13	20%MC + PLS		600	1170	180	-	-	0.5	0.55

The highest water-reducing effect was recorded when using PCE compared to additives based on naphthalene-formaldehyde and lignosulfonate. It was noted that the W/C ratio in compositions with SPNF-1 and PLS is approximately the same. With the introduction of MS into the system, water demand increases. This is due to the large adsorption capacity of the active mineral additive and the creation of additional areas on which superplasticizer molecules are deposited.

Previously, all the dry components are mixed, and a dry mixture is prepared, which is mixed with the mixing water in the following sequence (water is first poured into the mixing bowl):

- stirring for 120 s;
- stopping the mixer to remove the mixture stuck to the walls of the mixer bowl within 90 s;

- stirring for 60 s.

Beam samples with dimensions of $25 \times 25 \times 254$ mm were made from selected compositions of fine-grained concrete to determine the relative deformation.

The results of determining the relative deformation (Figure 2) showed that the introduction of plasticizer additives based on polycarboxylate esters and naphthalene formaldehydes contributes to an increase in the relative deformation, which indicates an intensification of the alkali-silicate reaction. If the deformation exceeds 0.1%, then the aggregate is considered potentially reactive with alkalis. The relative deformation (ε) of compositions with PCE and SPNF-1 exceeds the normalized value ε by 21 days. By day 28 for the composition with PCE, the relative deformation is the highest among all the studied superplasticizers and is more than 0.2%. This increase in relative deformation in concrete with PCE is associated with the uniform point distribution of the additive on cement particles, which does not interfere with the processes of hydration and saturation of the mixing water with Ca^{2+} , Na^+ , and K^+ ions, which, in contact with the reactive filler, form hydrosilicates of monovalent alkali metals. The increase in relative strain continues for 56 days, and in compositions with PCE, the values are the highest. The results obtained correlate with data from [12,27] and show that using NaOH in storage water, as carried out in these studies mentioned, does not mask the effect of SPNF.

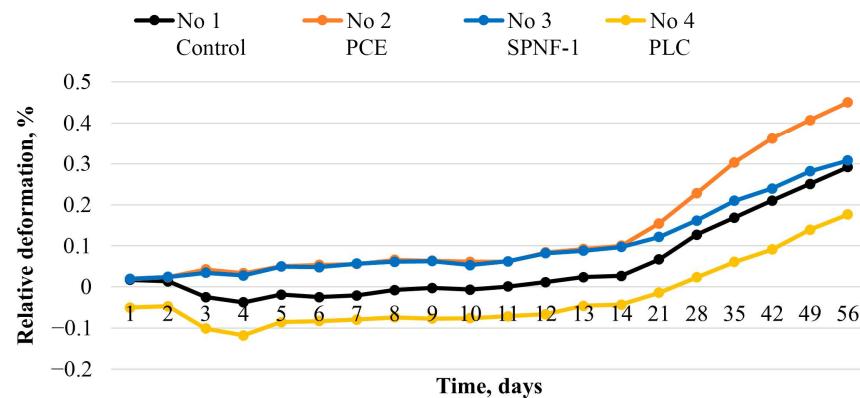


Figure 2. Relative deformation of concrete with various types of superplasticizing additives.

The use of the plasticizer PLS leads to negative values of relative deformations, which indicates blocking of the alkali-silicate reaction. The deformation processes are slowed down due to the adsorption of PLS on Portland cement particles and the formation of flocculi of particles, between which there is a very thin layer of hydrates, which reduces the rate of further hydration of cement particles, resulting in the blocking of the formation of alkalis Ca, Na, and K. After 28 days in compositions with PLS, an increase in relative deformation was recorded and lasted up to 56 days, but at the same time it also had the most minimal values. The reduced value of ε in compositions with PLS is explained by the property of lignosulfonates to slow down hydration processes.

A study of the concrete structure of the control composition No. 1 at the age of 28 days of hardening showed that the structure of calcium hydrosilicates contains a gel in the form of cracked plates and flakes up to $200 \mu\text{m}$ in size, which is a product of the “alkali-silicic acid” reaction. This indicates the presence of an alkali-silicate reaction in a concrete sample (Figure 3). By day 56, exposure to a 1 molar NaOH solution at a temperature of $+80^\circ\text{C}$ continued not only an increase in the amount of alkali-silicate gel but also its crystallization, with a decrease in the basicity and loose crystals of the alkali-silicate reaction are observed in PCE images (Figure 4).

A more dense and larger gel was formed from a mixture of sodium, potassium, and calcium hydrosilicates in compositions No. 2 with PSE and No. 3 with SPNF-1. The gradual formation of silicate gel in the hardened cement matrix increases internal stress due to the development of osmotic pressure, resulting in the formation of cracks (Figures 5 and 6).

The described process refers to internal corrosion processes and is associated with the interaction of cement alkalis with silica aggregates.

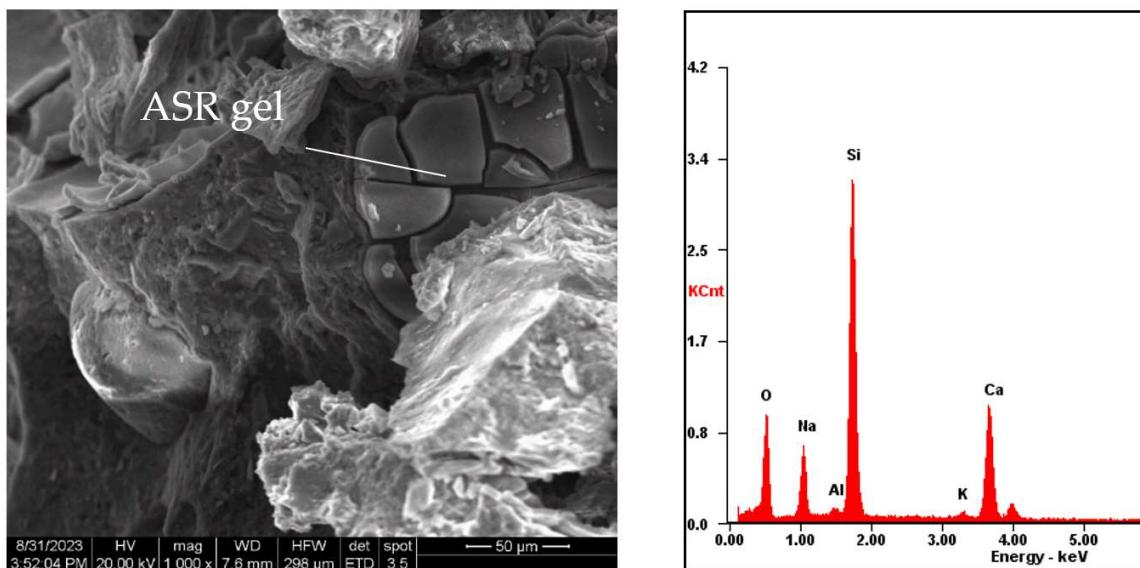


Figure 3. Microscopic image of a cracked gel in a microcrack of cement matrix, $\times 1000$, composition No. 1 control, 28 days.

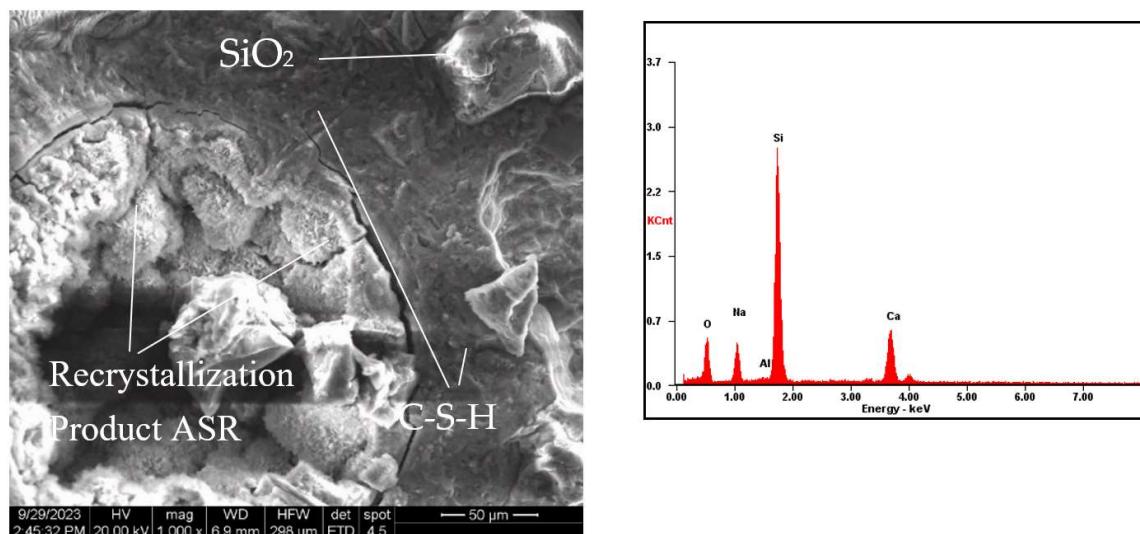


Figure 4. Microscopic image of a cracked gel in a microcrack of cement matrix, $\times 1000$, composition No. 1 control, 56 days.

Composition No. 4, with the addition of PLS (Figure 7), also contains a gel of hydrosilicates of monovalent alkali metals, but these hydrates are smaller in size and have a higher basicity (Figures 5 and 6).

By day 56, in compositions with plasticizers of different natures, not only an increase in the alkali-silicate gel was recorded, but a change in morphology and structure was observed. The alkali silicate gel became more textured and prone to recrystallization with an increase in the silicate component. In the composition with the addition of PCE (Figure 8), the silicate gel is denser and completely covers the silicon oxide grain compared to the compositions SPnf-1 (Figure 9) and PLS (Figure 10).

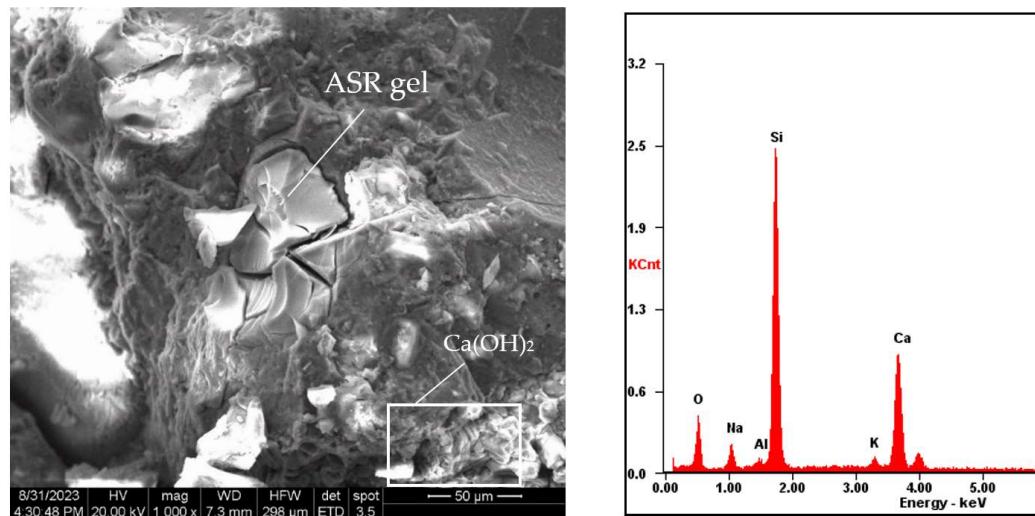


Figure 5. Microscopic image of a cracked gel in a microcrack of cement matrix, $\times 1000$, composition No. 2 with PCE, 28 days.

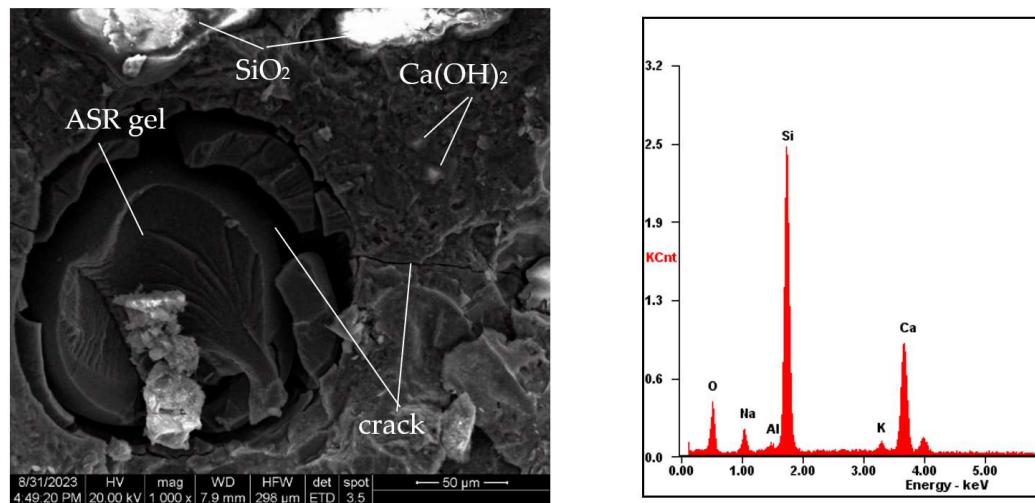


Figure 6. Microscopic image of a cracked gel in a microcrack of cement matrix, $\times 1000$, composition No. 3 with SPNF-1, 28 days.

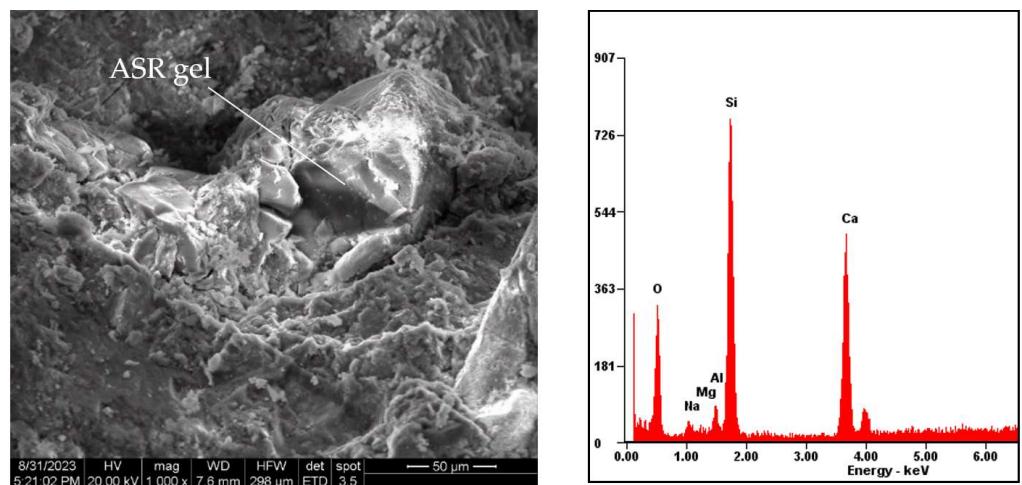


Figure 7. Microscopic image of a cracked gel in a microcrack of cement matrix, $\times 1000$, composition No. 4 with PLS, 28 days.

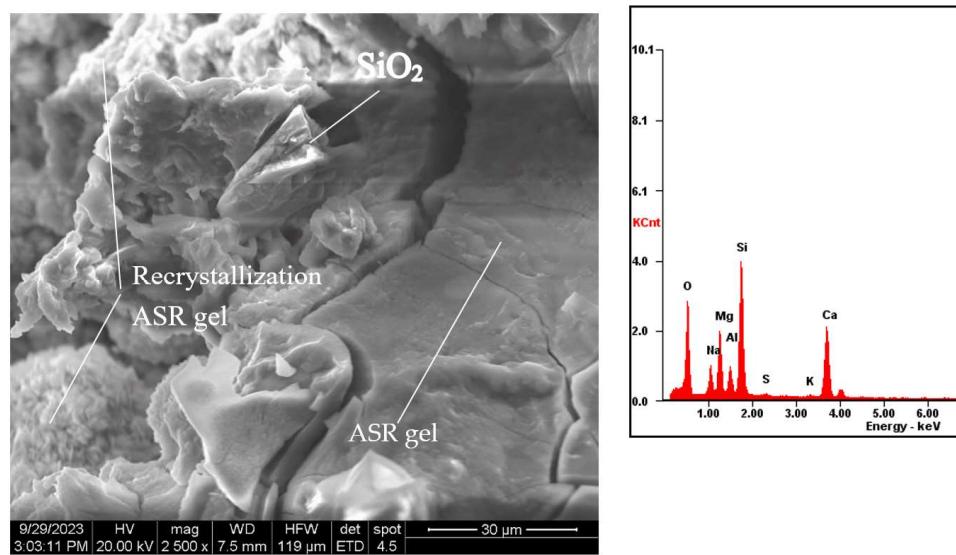


Figure 8. Microscopic image of gel formation around a grain of sand, $\times 2500$, composition No. 2 with PCE, 56 days.

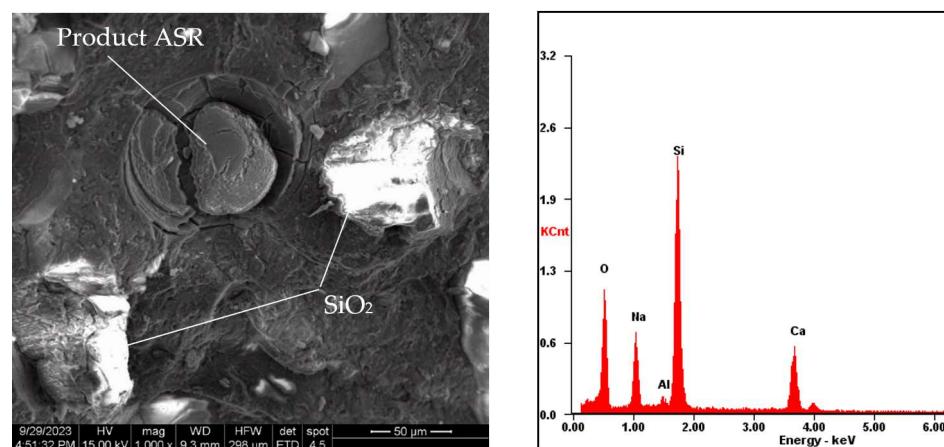


Figure 9. Microscopic image of a cracked gel in contact with grains of SiO_2 , $\times 1000$, composition No. 3 with SPNF-1, 56 days.

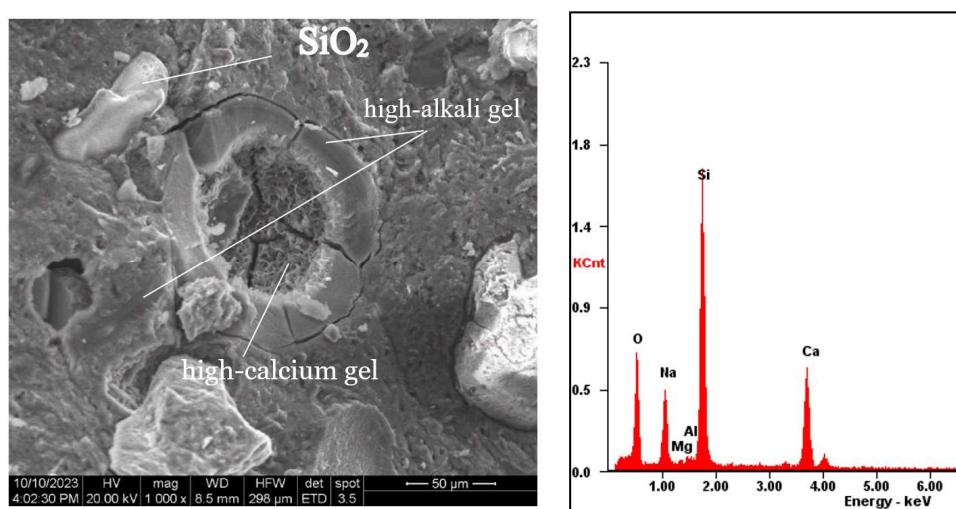


Figure 10. Microscopic image of a cracked gel in a cement matrix in contact with grains of SiO_2 , $\times 1000$, composition No. 4 with PLS, 56 days.

The XRF results also confirm the results of physical-mechanical tests and microscopic examination. During the process of hardening and storage in a 1 mol NaOH solution at +80 °C, the hydration process continues, as indicated by a decrease in the intensity of the peaks of the main clinker minerals in all compositions: alite C3S with d/n = 3.03; 2.77; 2.6 Å and belite C2S with d/n = 2.75; 2.71; 2.20; 1.93 Å, tricalcium aluminate with d/n = 4.08; 2.78; 1.9; 1.56; 1.35 Å and tetracalcium aluminum ferrite with d/n = 2.77; 2.63; 2.04; 1.92 Å. The diffraction patterns show a decrease in the intensity of the portlandite peaks with continued hydration processes and the appearance of silicate catoite peaks, the peaks of which are characteristic of a semi-amorphous substance. Catoite appears in the compositions after 7 days of storage in a 1 mol NaOH solution at +80 °C and does not increase quantitatively by 28 days, but an increase is observed by 56 days. The XRF results of compositions No. 1, No. 2, No. 3, and No. 4 on the 2nd day of hardening and on the 7th, 28th, and 56th days of storage in a 1 mol NaOH solution at +80 °C are presented in Figures 11–14.

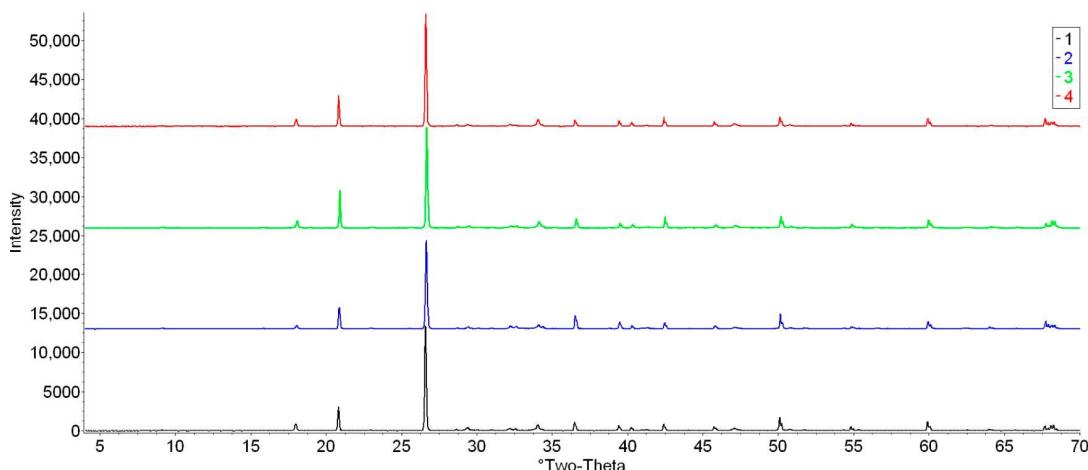


Figure 11. The recorded diffractograms of the mortar parts of concrete samples after 2 days of hardening.

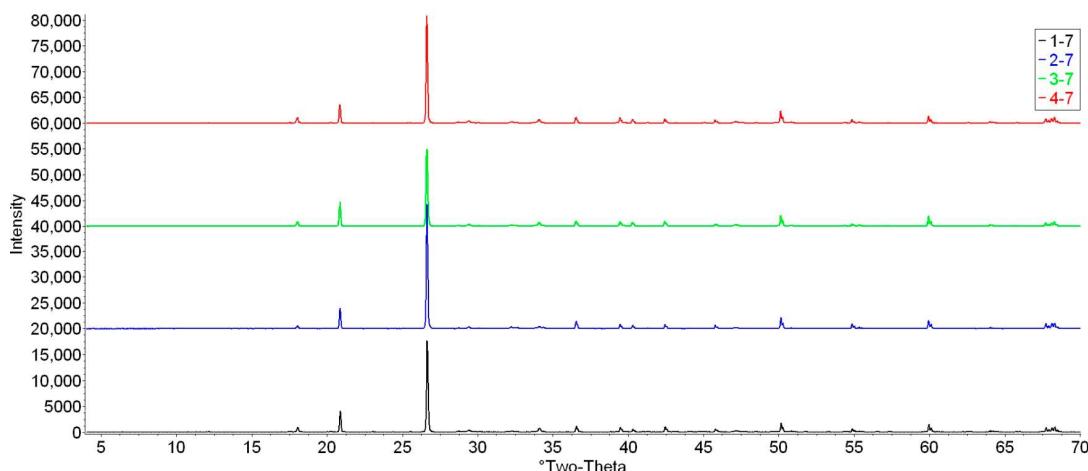


Figure 12. The recorded diffractograms of mortar parts of concrete samples after 7 days of holding in 1 N NaOH solutions at temperature +80 °C.

A study of the results of the relative deformation of compositions with MC together with superplasticizers of different natures showed that when the MC content is 30% for concrete with PCE and 20% and 30% for concrete with SPNF-1, the alkali-silicate reaction processes are stopped because no intensive expansion of samples was recorded up to 56 days, which is due to the binding of $\text{Ca}(\text{OH})_2$ into low-basic calcium hydrosilicates

(Figures 15 and 16). With a MC content of 10% for concrete with PCE, the relative deformations of concrete increase in the initial stages of hardening and reach a maximum at the age of 5 days with subsequent stabilization. With a MC content of 20% for concrete with PCE, the relative deformations after growth in the initial stages and stabilization upon reaching the age of 5 days resumed; at the age of 21 days, the relative deformations of concrete resumed growth (Figure 15). With a MC content of 10% for concrete with SPNF-1, the relative deformations after growth in the initial stages and stabilization upon reaching the age of 4 days, at the age of 14 days, resume growth (Figure 16). The increase in expansion strain when using silica fume is also confirmed by the authors of other studies [22,23,25,26].

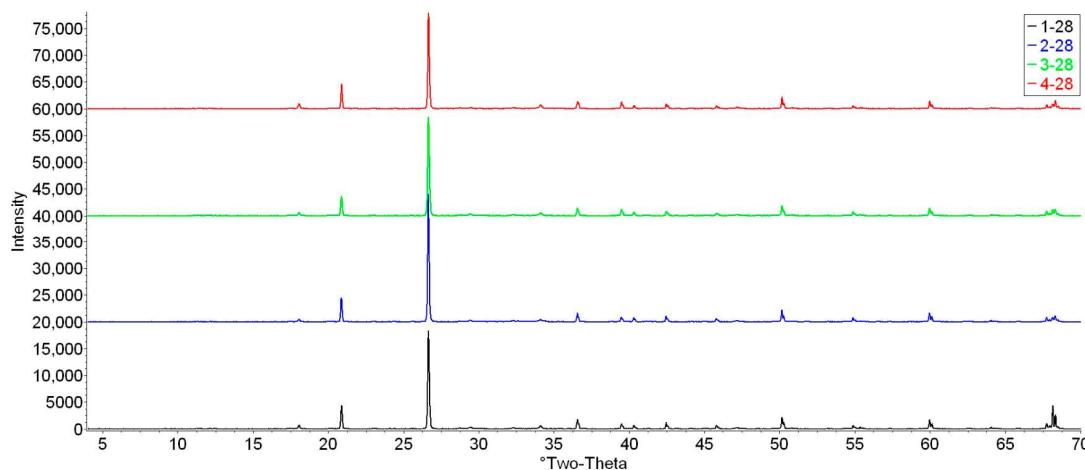


Figure 13. The recorded diffractograms of mortar parts of concrete samples, 28 days of holding in 1 N NaOH solutions at temperature +80 °C.

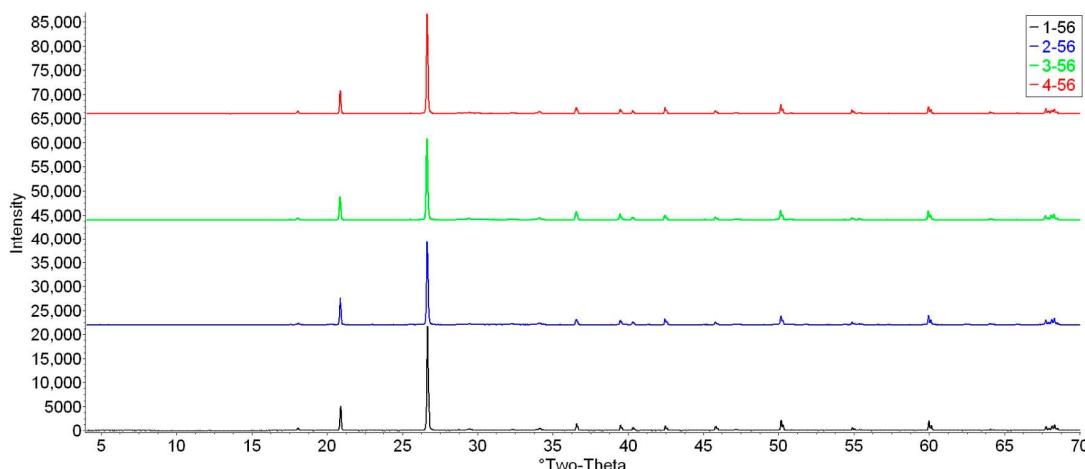


Figure 14. The recorded diffractograms of mortar parts of concrete samples, 56 days of holding in 1 N NaOH solutions at temperature +80 °C.

For concretes with PLS containing 10% and 30% MC, the increase in relative deformations begins at the age of 14 days. When the MC content is 20% in concrete with PLS, there are no relative deformations. For concrete with PLS, in the absence of MC in the composition, as noted above, at the age of 4 days, a maximum of shrinkage deformations is observed, followed by an increase in expansion deformations (Figure 17). This process possibly occurs due to the adsorption of the PLS additive not only on the mineral phases of cement but also on the particles of the mineral additive, which helps slow down the processes of the alkali-silicate reaction at an early age in concrete.

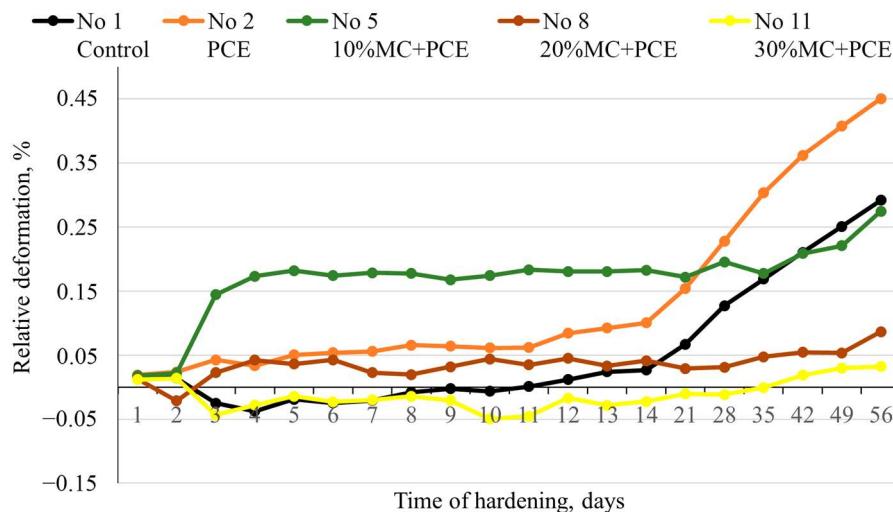


Figure 15. Influence of PCE and MC on relative deformation.

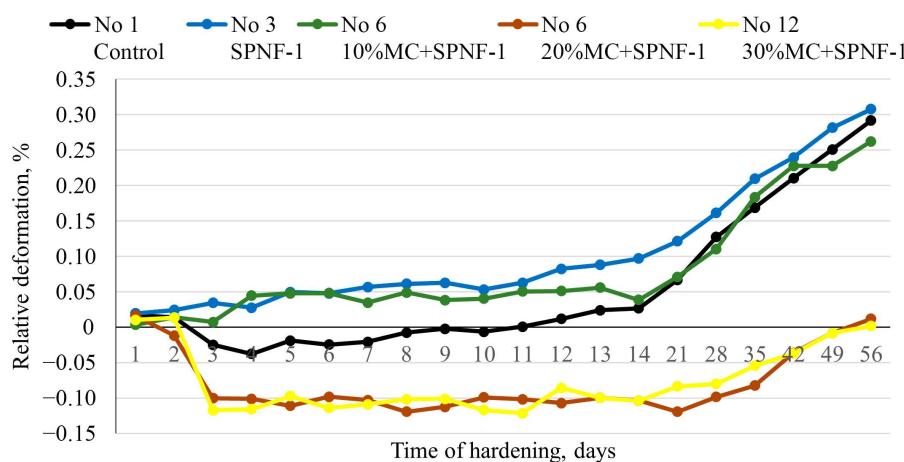


Figure 16. Influence of SPNF-1 and MC on relative deformation.

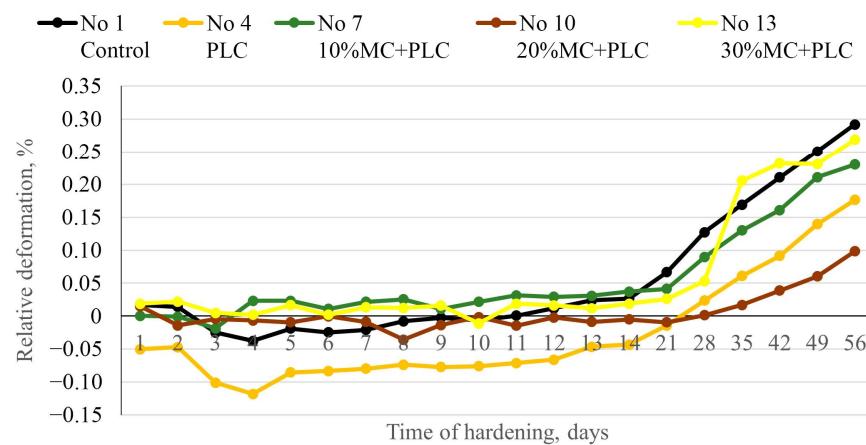


Figure 17. Influence of PLS and MC on relative deformation.

The study of the microstructural characteristics of concrete with the complex use of plasticizers with microsilica is in good agreement with the results of tests for determining relative deformation. At a dosage of MC in an amount of 30% with PCE (Figure 18a) and SPNF-1 (Figure 18b), by 7 days a dense structure with calcium hydrosilicates of low basicity is formed; non-hydrated cement grains are still present in the structure. By day 28, in a dense and well-crystallized structure, the presence of an alkali-silicate gel in the

composition with PCE and a cracked gel in the composition of SPNF-1 were already noted in the pores (Figure 18d,f).

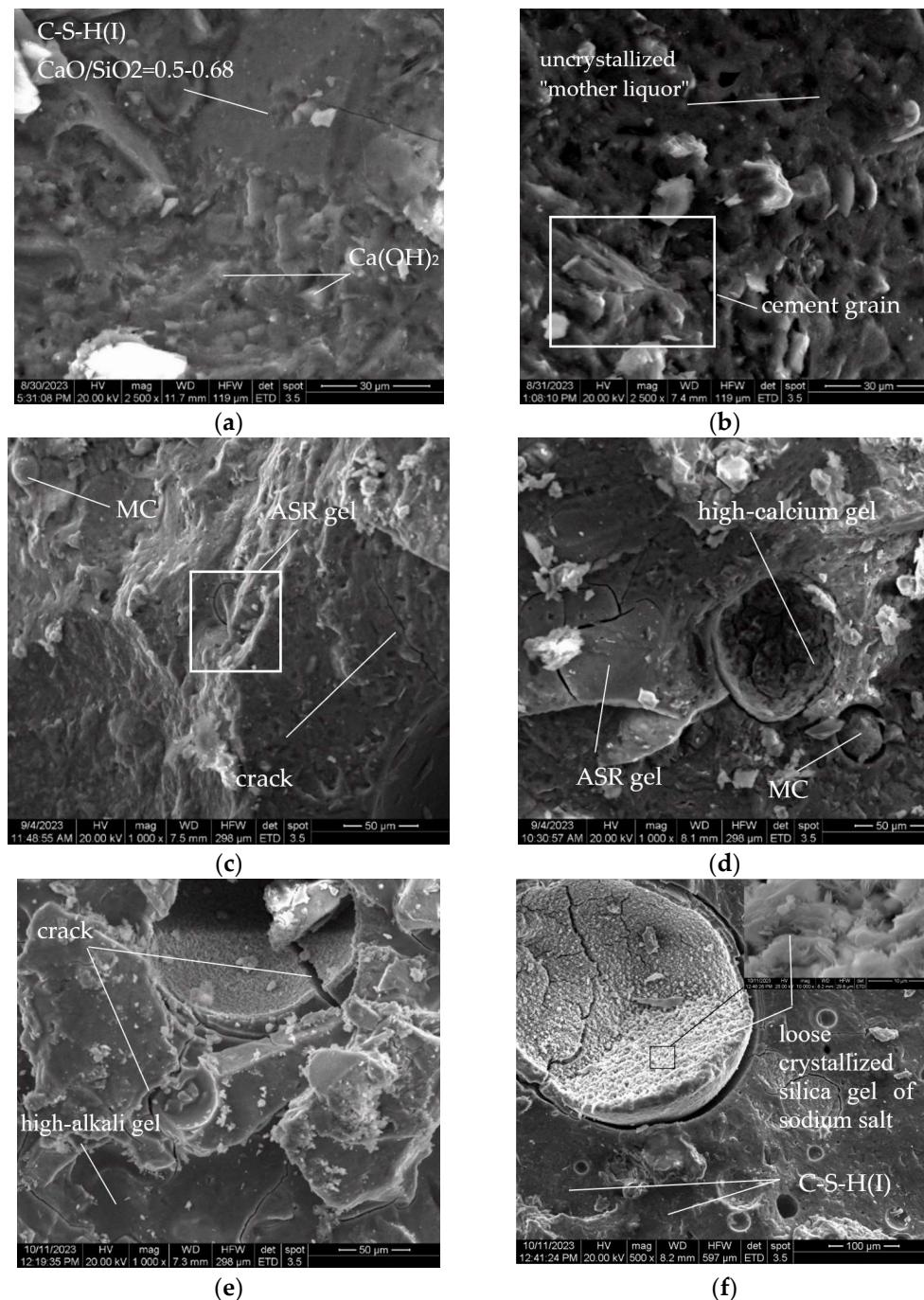


Figure 18. Microscopic images of cement matrix compositions with the complex additives MC + PCE and MC + SPNF-1. (a) 30%MC + PCE, 7 days, $\times 2500$; (b) 30%MC + SPNF-1, 7 days, $\times 2500$; (c) 30%MC + PCE, 28 days, $\times 1000$; (d) 30%MC + SPNF-1, 28 days, $\times 1000$; (e) 30%MC + PCE, 56 days, $\times 1000$; (f) 30%MC + SPNF-1, 56 days, $\times 500$ and $\times 10,000$.

By day 56 of storage, the structure of the composition with 30% MC and PCE (Figure 18e) is dense, homogeneous, and consists of low-basic calcium hydrosilicates, but an alkali silicate gel with low basicity begins to form in the pore space. The composition with SPNF-1 (Figure 18f) contains a loosely crystallized silicate gel of sodium salt in the structure of which there are fine-crystalline hexagonal hydrates in the form of small spherulites

and monosulfate forms of calcium hydrosulfoaluminates; these hydrates under humid conditions can recrystallize into more perfect and larger ettringite crystals, which can cause additional internal stresses, which can lead to the formation of cracks in the cement stone.

A study of the microstructure of the sample with the combined use of PLS with MC shows that at the age of 7 days at dosages of MC of 10% and 20%, the development of an alkali-silicate reaction is not observed, but when the amount of MC is increased to 30%, a cracked silicate gel is observed (Figure 19).

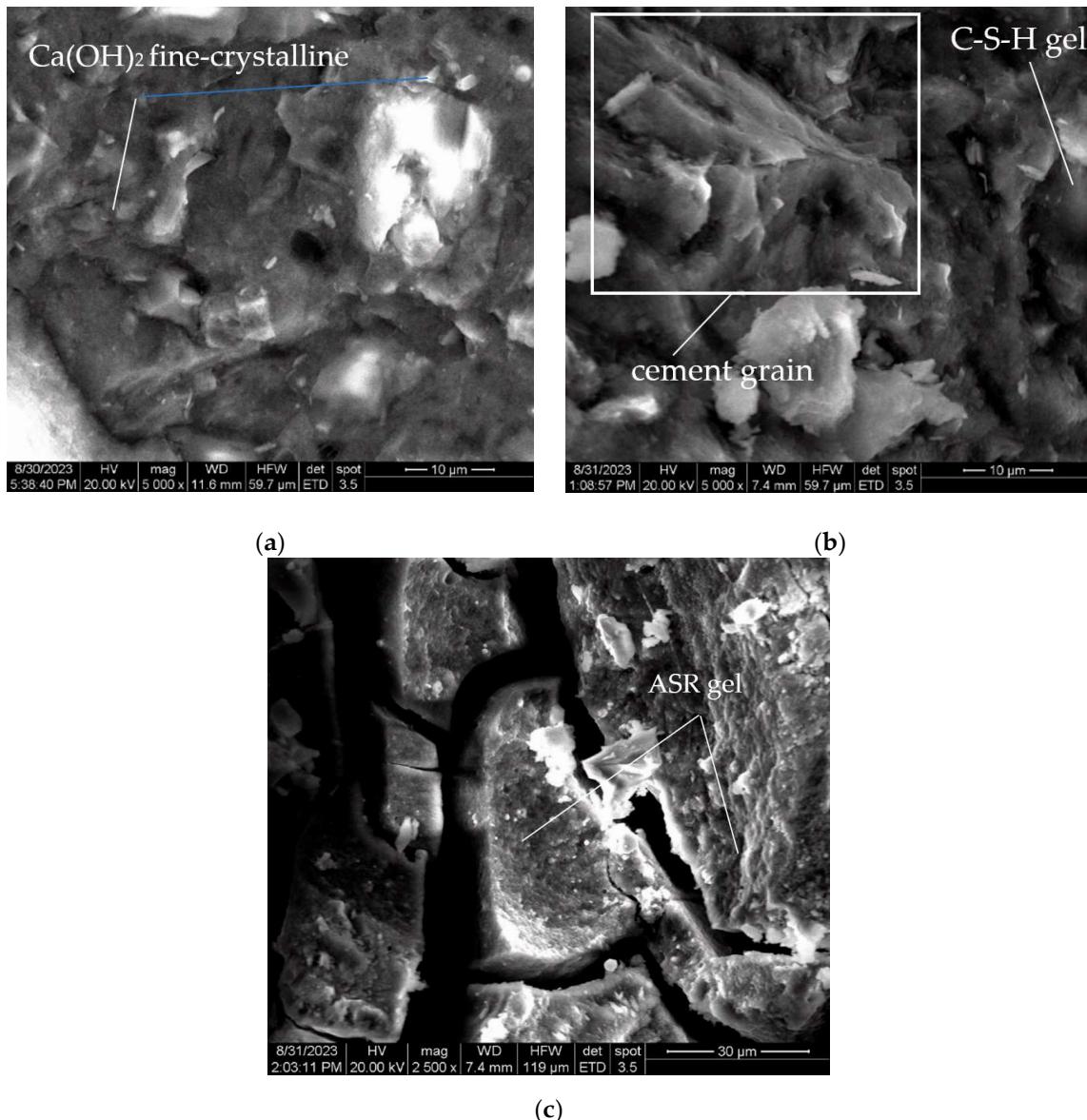


Figure 19. Microscopic images of cement matrix compositions with a complex additive MC + PLS, 7 days. (a) 10% MC + PLS; (b) 20% MC + PLS; (c) 30% MC + PLS, $\times 2500$.

By the 28th day of hardening, when PLS is used together with MC (Figure 20) at dosages of 10% and 20%, at the initial stage the formation of non-textured products of the alkali-silicate reaction is observed, and with an increase in microsilica to 30%, local alkali-silicates are formed in the concrete mixture. silicate gel inclusions with many small cracks, as can be seen in Figure 20c. Considering the above data, it can be assumed that the introduction of MC in combination with PLS does not stop the alkaline reactivity but only slows it down in the initial stages. Perhaps this effect occurs because PLS slows down the hydration processes [41], at which point the pH of the environment does not increase

and the formation of alkalis Ca and Na (mostly) stops, thereby preventing the intensive formation of alkaline corrosion products. And when MC is introduced into the system, on the contrary, hydration processes are accelerated, which leads to an imbalance in the pH of the environment since some of the cement alkalis do not have time to combine with MC and can freely bind to reactive silica. In the available literature, there is quite a bit of information about the use of plasticizing additives based on lignosulfonates, especially the study of their effect on alkaline corrosion. Therefore, the data obtained can be used in the future to produce concrete that is more resistant to corrosion.

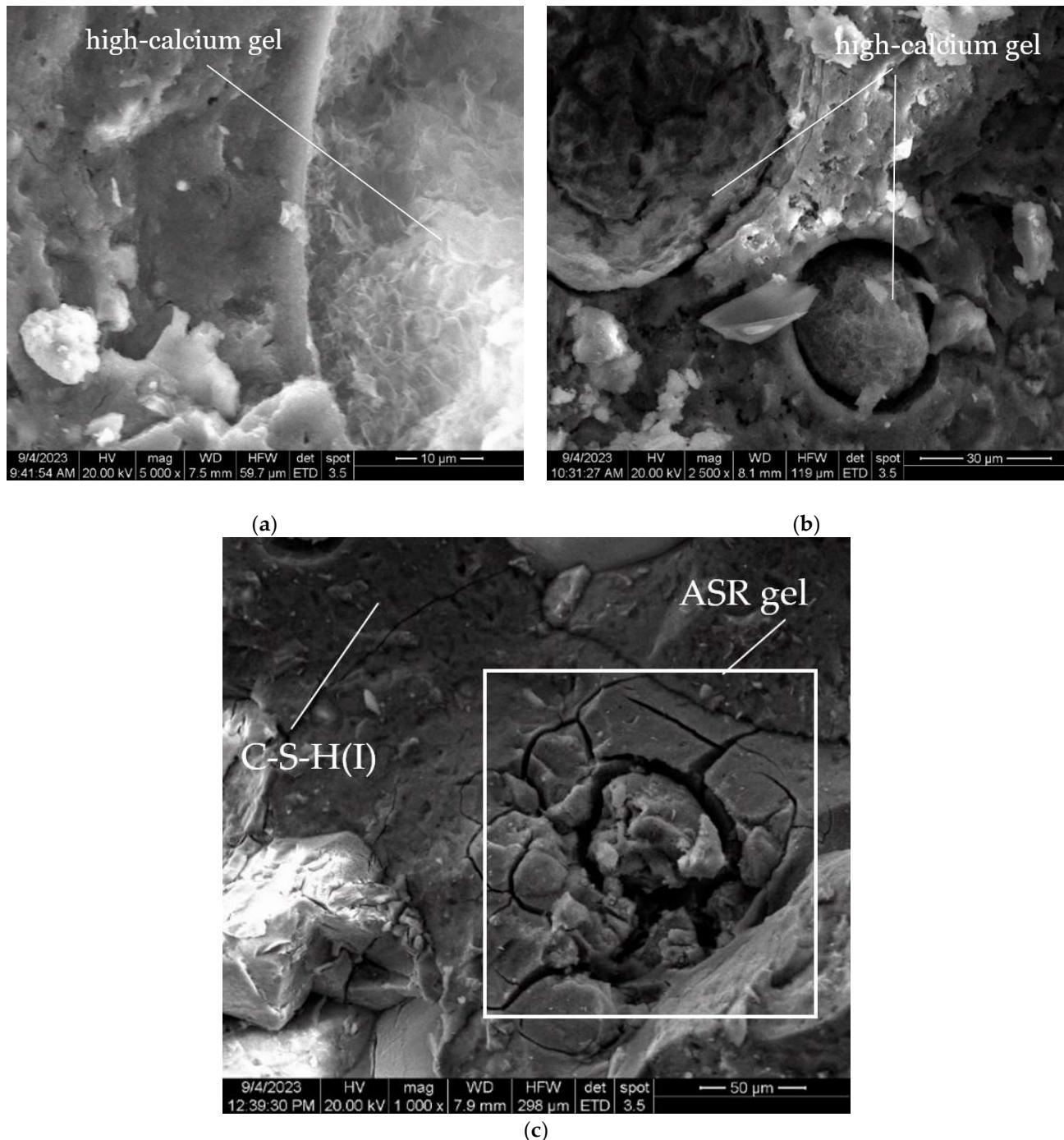


Figure 20. Microscopic images of cement matrix compositions with a complex additive MC + PLS, 28 days. (a) PLS + 10%MC, $\times 5000$; (b) PLS + 20%MC, $\times 2500$; (c) PLS + 30%MC, $\times 1000$.

After 56 days, in compositions with 30% MC and PLS (Figure 21), the areas of formation of the alkali-silicate gel enlarge, and with an increase in the dosage of MC to 30%, large-scale formation of spheres consisting of gel-like and crystallized products of the alkali-silicate reaction occurs. These crystals, gels, and spheres are interconnected by a web of cracks, which are destructive points and areas of cement, stone, and concrete in general.

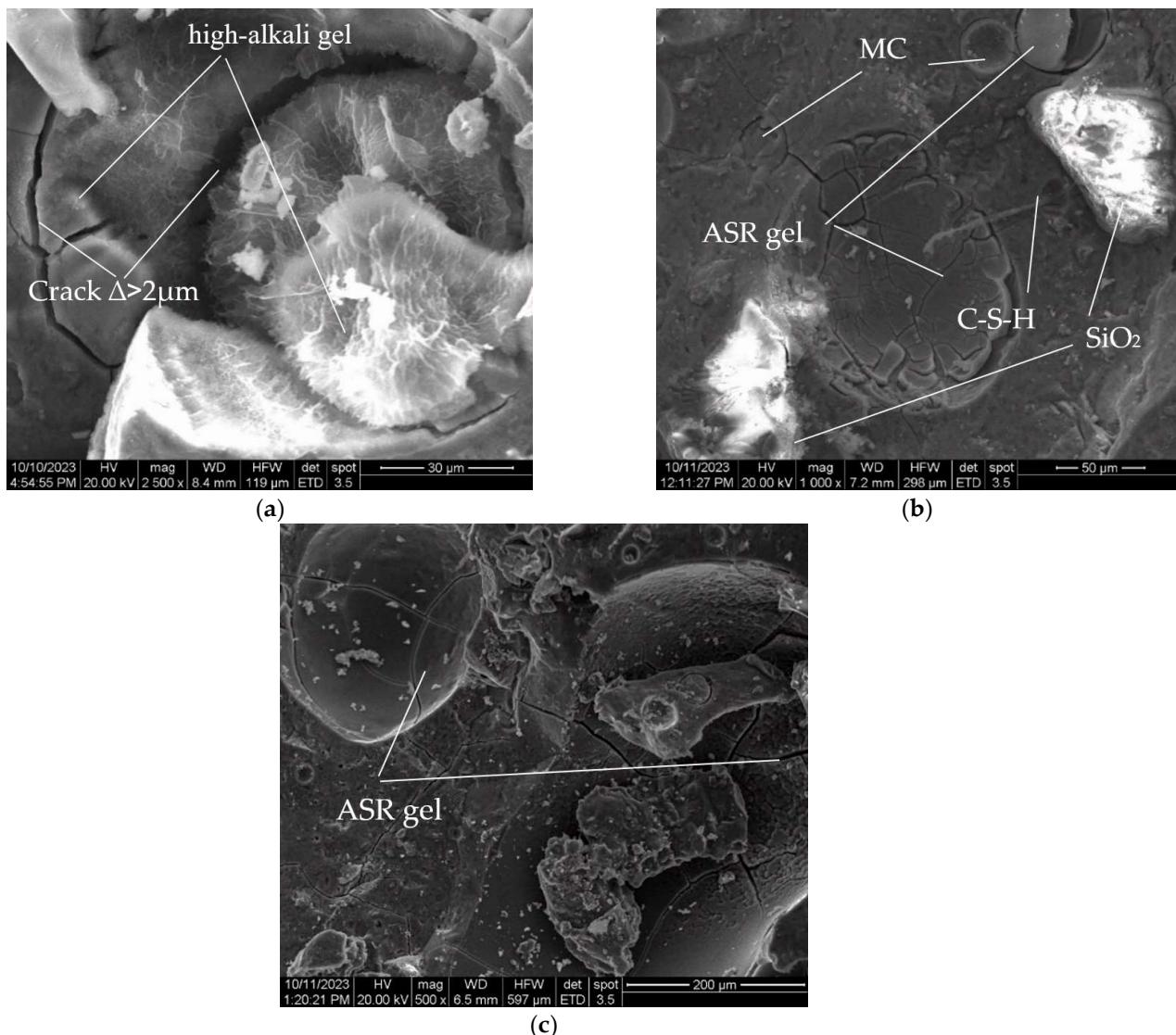


Figure 21. Microscopic images of cement matrix compositions with a complex additive MC + PLS, 56 days. (a) PLS + 30%MC, $\times 2500$; (b) PLS + 30%MC, $\times 1000$; (c) PLS + 30%MC, $\times 500$.

4. Conclusions

This research work showed that superplasticizers widely used in the construction industry not only improve technological properties but also affect the process of internal alkaline corrosion.

The analysis of the data obtained in this study enables us to draw the following conclusions: The use of superplasticizers based on polycarboxylate and naphthalene-formaldehyde does not stop the alkali-silicate reaction but only has an inhibitory effect in the initial stages of hardening; at the age of 28 days, an increase in deformations and an increase in the value of the relative deformation are noted. By the 56th day of storage, the increase in relative strain with SPNF and PCE additives is higher at 15% and 50%, respectively. The use of an additive based on lignosulfonates stops deformation changes

in the initial stages of hardening, but only after 21 days. There is an increase in relative deformation and an increase in the value of relative deformation.

When MC and various types of superplasticizers are used together in a concrete mixture, the development of ASR, depending on the dosage of MC and the type of superplasticizer, has significant differences. When using MC with PCE, the effect of reducing deformations from the use of an active mineral additive appears only at a dosage of 30%. At dosages of 10% and 20%, deformation changes do not slow down but, on the contrary, exceed the standard value of 0.1%. The combined use of MC and SP makes it possible to achieve the effect of reducing deformations already at a dosage of microsilica of 20%. The use of MC together with PLS does not have a significant effect on deformation compared to the control concrete sample; however, MC increases the value of the relative deformation compared to concrete with only the addition of PLS. This effect is probably due to the retarding effect of PLS on the hydration of Portland cement. Because of this process, an increase in relative deformations occurs only after 21 days, and on the 56th day, it approaches the value of the relative deformation of the control sample.

XRD analysis of concrete showed that MC particles likely react with cement alkalis much faster than active silica present in aggregates. A competitive reaction and limitation of the formation of an alkali silicate gel in the contact zone of aggregates and cement stone are observed when MC is used together with PCE and SPNF-1 at MC dosages of 20% or more. When dosages of MC are 10% and combined with the superplasticizers SPCE, SP, and PLS, free alkalis appear, the content of which grows with increasing hydration, which promotes the growth of alkali-silicate reaction products in concrete.

The obtained relationships between the content of plasticizer, microsilica, and relative deformation and structural changes allow us to identify the composition most resistant to ASR. Such compositions are mixtures containing the plasticizers SPNF, PCE, and MC by more than 20%.

Limitations of this Study

- Data collection and analysis relate only to the topic of the research being conducted.
- Relatively short observation period.
- Application of an accelerated test method by storing in a solution with an increased pH.

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References

1. Stanton, T.E. Influence of cement and aggregate on concrete expansion. In *Engineering News-Record*; McGraw-Hill: New York, NY, USA, 1940; pp. 59–61.
2. Stanton, T.E. Expansion of concrete through reaction between cement and aggregate. *Proc. Am. Soc. Civ. Eng.* **1940**, *66*, 1781–1811. [[CrossRef](#)]
3. Ivanov, F.M.; Lobarskaya, G.V.; Rosental, N.K. Interaction of concrete aggregates with cement alkalis and additives. *Concr. Reinforced Concr.* **1995**, *1*, 15–18.
4. Moskvin, V.M.; Royak, G.S. *Corrosion of Concrete under the Action of Cement Alkalies on Aggregate Silica*; Gosstroyizda: Moscow, Russia, 1962; 164p.

5. Yan, Y.; Yang, S.Y.; Miron, G.D.; Collings, I.E.; L'Hôpital, E.; Skibsted, J.; Winnefeld, F.; Scrivener, K.; Lothenbach, B. Lothenbach Effect of alkali hydroxide on calcium silicate hydrate (C-S-H). *Cem. Concr. Res.* **2022**, *151*, 106636. [[CrossRef](#)]
6. Bagheri, M.; Lothenbach, B.; Scrivener, K. Scrivener The effect of paste composition, aggregate mineralogy and temperature on the pore solution composition and the extent of ASR expansion. *Mater. Struct.* **2022**, *55*, 192. [[CrossRef](#)]
7. Davidyuk, A.N.; Orlov, A.D.; Davidyuk, A.A. Method of making a mixture for alkaline corrosion resistant lightweight concrete. Application No. 2021139673 RU 2788912 C1, 25 January 2023. Available online: <https://findpatent.ru/patent/278/2788912.html> (accessed on 8 November 2023).
8. Ustyugov, A.S.; Chelovan, I.S.; Shepelenko, T.S. Corrosion resistance of a modified cement composite in an aggressive environment. In *Selected reports of the 68th University Scientific and Technical Conference of Students and Young Scientists*; Tomsk State University of Architecture and Civil Engineering: Tomsk, Russia, 2022; pp. 506–508.
9. Rajabipour, F.; Giannini, E.; Dunant, C.; Ideker, J.H.; Thomas, M.D. Thomas Alkali—Silica reaction: Current understanding of the reaction mechanisms and the knowledge gaps. *Cement Concr. Res.* **2015**, *76*, 130–146. [[CrossRef](#)]
10. Qiu, X.; Chen, J.; Ye, G.; De Schutter, G. De Schutter Insights in the chemical fundamentals of ASR and the role of calcium in the early stage based on a 3D reactive transport model. *Cement Concr. Res.* **2022**, *157*, 106778. [[CrossRef](#)]
11. Rakhrinbaev, S.M.; Tolipina, N.M.; Bales, A.A. The influence of plasticizer additives on internal corrosion of concrete. *Innov. Mater. Technol. Omsk* **2013**, *4*, 195–197.
12. Leemann, A.; Lothenbach, B.; Thalmann, C. Influence of superplasticizers on pore solution composition and on expansion of concrete due to alkali-silica reaction. *Constr. Build. Mater.* **2011**, *25*, 344–350. [[CrossRef](#)]
13. Kochetkov, A.V.; Yankovskiy, L.V. Project for flexible production of multicomponent mixtures of deicing materials. Transport. Transport facilities. *Ecology* **2014**, *1*, 65–78.
14. Antolik, A.; Jozwiak-Niedzwiedzka, D. Assessment of the alkali-silica reactivity potential in granitic rocks. *Constr. Build. Mater.* **2021**, *295*, 123690. [[CrossRef](#)]
15. Romenenko, I.I. Resistance of aggregates in cement stone in ensuring the durability of structures. *Reg. Archit. Constr.* **2019**, *2*, 32–38.
16. Kramar, L.Y.; Trofimov, B.Y.; Gamaliy, E.A.; Chernih, T.N.; Zimin, V.V. *Modifiers for Cement Concrete and Mortars (Technical Characteristics and Mechanism of Action)*; Pero: Chelyabinsk, Russia, 2012; 202p.
17. Usherov-Marshak, A.B. *New Generation Supplements*; Colorit: Kharkov, Ukraine, 2005; pp. 45–50.
18. Carrasquillo, R.L.; Snow, P.G. Effect of fly ash on alkali-aggregate reaction in concrete. *Mater. J.* **1987**, *84*, 299–305.
19. ACI 234R-06; Guide for the Use of Silica Fume in Concrete. ACI: Indianapolis, IN, USA; p. 63.
20. Nagrockienė, D.; Rutkauskas, A. The effect of fly ash additive on the resistance of concrete to alkali silica reaction. *Constr. Build. Mater.* **2019**, *201*, 599–609. [[CrossRef](#)]
21. Žvironaitė, J.; Malaishkenė, J.; Pranckevicienė, J.; Shkamat, E.; Stonis, R. The influence of mineral additives on the development of alkali corrosion in Portland cement concrete with reactive gravel filler. *Cem. Its Appl.* **2020**, *2*, 64–69.
22. Lindgard, J. Alkali-silica reactions (ASR): Literature review on parameters influencing laboratory performance testing. *Cem. Concr. Res.* **2012**, *42*, 223–243. [[CrossRef](#)]
23. Diamond, S. Alkali-aggregate reactions in concrete—Pore solution effects. In Proceedings of the 6th International Conference on AAR in Concrete, Denmark, Copenhagen, 22–25 June 1983; pp. 155–167.
24. Duchesne, J.; Béribé, M.A. Effectiveness of supplementary cementing materials in suppressing expansion due to ASR: Part 2 Effect on the pore solution chemistry. *Cem. Concr. Res.* **1994**, *24*, 221–230. [[CrossRef](#)]
25. Sorvacheva, Y.A.; Petrova, T.M. The influence of the granulometric composition of metakaolin on the inhibition of the alkali-silicate reaction. *Cem. Its Use* **2014**, *3*, 102–106.
26. Shehata, M.H.; Thomas, M.D. Use of ternary blends containing silica fume and fly ash to suppress expansion due to alkali-silica reaction in concrete. *Cem. Concr. Res.* **2002**, *32*, 341–349. [[CrossRef](#)]
27. Sorvacheva, Y.A.; Petrova, T.M.; Gibson, K.; Fedchenko, A.A. The influence of superplasticizers based on polycarboxylates on alkali silicate expansion of concrete. *Constr. Mater.* **2014**, *5*, 15–21.
28. Bazhenov, Y.M.; Demyanova, V.S.; Kalashnikov, V.I. *Modified High Quality Concrete*; Publishing House of the Association of Construction Universities: Moscow, Russia, 2006; 368p.
29. Ratinov, V.B.; Rosenberg, T.I. *Additives to Concrete*; Stroyizdat: Moscow, Russia, 1989; 188p.
30. Demyanenko, O.V.; Kopanitsa, N.O.; Sarkisov, Y.S.; Gorshkova, A.V. Cement compositions modified with combined nanodispersed additives. *Bull. Tomsk. State Univ. Archit. Civ. Eng.* **2017**, *4*, 101–110.
31. Lothenbach, B.; Winnefeld, F.; Figi, R. The influence of superplasticizers on the hydration of Portland cement. In Proceedings of the 12th International Congress on the Chemistry of Cement, Montreal, QC, Canada, 8–13 July 2007. W1-05.3.
32. Schwarz, W. Novel cement matrices by accelerated hydration of the ferrite phase in Portland cement via chemical activation: Kinetics and cementitious properties. *Adv. Cem. Based Mater.* **1995**, *2*, 189–200. [[CrossRef](#)]
33. Paul, E. Influence of superplasticizer on workability and strength of ambient cured alkali activated mortar. *Clean. Mater.* **2022**, *6*, 100152. [[CrossRef](#)]
34. Hemstad, P.; Zuschlag, P.; Kjellemyr, P.; Lindgård, J.; Kjellsen, K.O.; Rønning, T.F.; Justnes, H.; De Weerdt, K. Alkali Metal Distribution in Composite Cement Pastes and its Relation to Accelerated Asr Tests (under review). *Cem. Concr. Res.* **2023**, *173*, 107283. [[CrossRef](#)]

35. Uchikawa, H.; Hanehara, S.; Sawaki, D. The role of steric repulsive force in the dispersion of cement particles in fresh paste prepared with organic admixtures. *Cem. Concr. Res.* **1997**, *27*, 37–50. [[CrossRef](#)]
36. Kim, B.G.; Jiang, S.J.; Aïtcin, P.C. Influence of molecular weight of PNS superplasticizers on the properties of cement pastes containing different alkali contents. In *The Role of Admixtures in High Performance Concrete*; Cabrera, J.G., Rivera-Villarreal, R., Eds.; RILEM Proceedings PRO5; RILEM Publications: Champs sur Marne, France, 1999; pp. 97–111.
37. ASTM C 227-03; Standard Test Method for Potential Alkali Reactivity of Cement–Aggregate Combinations (Mortar-Bar Method). Annual Book of ASTM Standards: West Conshohocken, PA, USA, 2004; pp. 141–145.
38. Wang, H.; Gillott, J.E. The effect of superplasticizers on alkali-silica reaction. In Proceedings of the 8th International Conference on Alkali-Aggregate Reaction, Kyoto, Japan, 17–20 July 1989; pp. 187–192.
39. ASTM C 1260-23; Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method). Annual Book of ASTM Standards: West Conshohocken, PA, USA, 2023; p. 5.
40. Tosun, K.; Felekoglu, B.; Baradan, B. The effect of cement alkali content on ASR susceptibility of mortars incorporating admixtures. *Build. Environ.* **2007**, *42*, 3444–3453. [[CrossRef](#)]
41. Eleneva, A. Development of a Complex Additive for Accelerated Hardening of Cement Stone. Ph.D. Thesis, Mendeleev University of Chemical Technology of Russia, Moscow, Russia, 2017; 17p. Available online: https://diss.muctr.ru/media/dissertations/2017/04/%D0%94%D0%B8%D1%81%D1%81%D0%B5%D1%80%D1%82%D0%B0%D1%86%D0%B8%D1%8F_%D0%95%D0%BB%D0%B5%D0%BD%D0%BE%D0%B2%D0%B0_%D0%90.%D0%90..pdf (accessed on 8 November 2023).

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