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The Resistance of New Kind of High-Strength Cement after 5 Years Exposure to Sulfate Solution

Michal Bačuvčík, Pavel Martauz, Ivan Janotka and Branislav Cvopa

Abstract

This article deals with the determination of technically important properties, the recognition of microstructure and pore structure, and the mortar resistance of a new cement kind NONRIVAL CEM I 52.5 N containing 7.94% wt. of C_3A to 5% sodium sulfate solution. Both reference types of cement were industrially manufactured: 1) ordinary Portland cement CEM I 42.5 R and 2) Portland cement CEM I 42.5 R – SR 0, declared as sulfate resistant because of $C_3A = 0\%$. The research was carried out at standardized mortars. The used sodium sulfate solution, which contained 33802.8 mg of aggressive SO_4^{2-} per liter, exceeded approximately 5 to 10 times the concentration of the third degree of aggressiveness of the XA chemical environment according to STN EN 206 + A1. The reference medium was drinking water. The 5-year results of non-destructive and destructive physical-mechanical tests as well as the formed microstructure and pore structure in both liquid media were evaluated. The cause of the NONRIVAL CEM I 52.5 N sulfate resistance was explained, despite the manufacturer's declared C_3A content of up to 8% by weight. Sulfate resistance of NONRIVAL CEM I 52.5 N is found comparable to that of sulfate resistant CEM I 42.5 R – SR 0.

Keywords: high-strength cement, sulfate resistance, durability

1. Introduction

A sulfate attack represents one of the most aggressive ways of acting on concrete, which worsens the durability of the structures. There is a large number of civil engineering structures, such as the foundations of pillars, bridges or concrete canals, etc., which could be exposed to aggressive sulfates throughout their lifetime [1–3]. The resistance of concrete is increased by using durable types of cement compared to Portland, such as pozzolanic cement when natural or industrial pozzolans are added. Považská cementáreň a. s., Ladce has developed a new type Portland cement, designated as NONRIVAL CEM I 52.5 N, which does not meet the criteria for sulfate-resistant cement according to the requirements of STN EN 197–1 [4]. NONRIVAL CEM I 52.5 N is considered to

be an innovative new generation cement [5] with a content of up to 5% wt. of industrially produced submicron-sized pozzolanic addition with minimum of 50% SiO₂. Studies show that the response of a cement-based material to sulfate attack varies in many cases and is influenced by many factors. Most experiments took place on a macroscopic scale, but it should be noted that the essence of the resulting attack lies in changes in the microstructure and pore structure of the cement matrix. Therefore, it is necessary to study the sulfate attack on cement-based mortar not only by assessing its physical properties but also by analyzing a microstructure and pore structure [6]. The condition of the pore structure of concrete is an important criterion for assessing sulfate resistance as its strength, as it determines the permeability for the penetration of aggressive solution into the interior of the microstructure formed over time.

According to the source of sulfate ions, sulfate attack is divided into two main types by secondary ettringite formation: external and internal. External sulfate attack occurs when the source of sulfates comes from the external environment when sulfates penetrate the concrete structure. Internal sulfate attack is caused by internal sulfate sources in an environment without external sulfate sources, such as coming from aggregates or by the thermal decomposition of ettringite [7].

External sulfate attack, also referred to as traditional, is characterized by the chemical interaction of sulfate-rich soil or water with the hydrated cement matrix. Soils containing sodium, potassium, magnesium, and calcium sulfates are the main sources of sulfate ions in groundwater. Another source of sulfates is industrial wastewater, e. g. from the chemical or agricultural industry [8–10].

External sulfate attack occurs if the following three factors coexist:

- a. high permeability of the cement composite/concrete structure;
- b. sulfate-rich environment;
- c. the presence of water.

The first step of the external sulfate attack is the penetration of sulfate ions from the outer environment into the concrete. Consequently, the transformation of calcium hydroxide and/or calcium silicate hydrate (C-S-H) to gypsum takes place according to specific reactions [11]. This process causes the hydrated cement matrix to expand, crack, and peel. Gypsum is prevalingly formed by the reaction of sulfate ions with Ca(OH)₂ or calcium silicate hydrate (C-S-H). However, a more important manifestation of sulfate attack is the reduction of the strength and cohesiveness of the developed cement matrix by the decalcination of C-S-H.

The STN EN 197–1 [4] defines sulfate-resistant cement for general use as a cement whose properties meet the requirements for sulfate resistance. Additional requirements for sulfate-resistant cement are the sulfate content (as SO₃) in cement, the C₃A content in clinker, and the pozzolanicity of cement. The seven sulfate-resistant cements for general use are divided into 3 main types as follows:

1. Sulfate-resistant Portland cement with different C₃A content in clinker:
 - C₃A content in the clinker = 0% by weight, designated as CEM I-SR 0
 - C₃A content in the clinker ≤3% by weight, designated CEM I-SR 3
 - C₃A content in the clinker ≤5% by weight designated CEM I-SR 5;

2. Sulfate-resistant blast furnace cement without the requirement for C_3A content in clinker: either designated CEM III/B-SR or CEM III/C-SR;
3. Sulfate-resistant pozzolanic cement with C_3A content in a clinker $\leq 9\%$ by weight: designated either CEM IV/A-SR or CEM IV/B-SR.

Sulfate-resistant types of cement, defined by the European standards [12, 13] must therefore meet the criteria for C_3A , SO_3 , and pozzolan content, without additional requirements for verifying their resistance. The standards discriminate “new generation cements”, which, despite not meeting the criteria in the defined standards, can show high sulfate resistance. Other ways to increase sulfate resistance are “innovative cement kinds” either hybrid cement [14] or as in this case, high-fine pozzolanic addition present in the cement. Such a cementitious composition with active submicron-sized pozzolanic particles forms a dense microstructure, poor in $Ca(OH)_2$ but rich in gel hydration products that are specified by low-permeable pore structure.

There are various ways to verify chemical resistance; a) long-term, multi-year exposures to aggressive media [15, 16] and b) accelerated [17, 18]. However, there is no known, unified and universally valid testing methodology worldwide. Therefore, the efficiencies of determinations are not mutually comparable; in addition, the same material systems and exposure conditions are not always tested. The final output of each method is a knowledge on the increased chemical (e. g. sulfate) resistance of the verified cement system compared to the reference. It is still problematic to determine the coherence between the laboratory test results (a or b) and the actual resistance time of concrete used in the field for decades of years either in aggressive soil or groundwater.

The objective of this chapter is to characterize the sulfate resistance of submicron-sized pozzolan containing NONRIVAL CEM I 52,5 N with up to 8% wt. C_3A and to explain the cause for its comparability with sulfate-resistant CEM I 42.5 SR 0 with none of C_3A .

2. Experimental procedure

2.1 Materials

Ordinary Portland cement (CEM I 42.5 N) as a reference cement 1 (PC), sulfate-resistant CEM I 42.5 R - SR 0 as a reference cement 2 (SR) and NONRIVAL CEM I 52.5 N as experimental cement (N), were used. Both reference types of cement were produced according to STN EN 197-1 [4] and NONRIVAL CEM I 52.5 N was prepared according to the internal cement plant's standard and SK technical assessment.

2.2 Casting and curing

Mortar specimens of size (40 × 40 × 160) mm with the cement to standard sand weight ratio of 1: 3 and water to cement ratio of 0.5, were prepared. The mortars were cured 24 hours at 20°C/95% R.H.-air in a climate chamber. After demolding, they were kept 27 days in water at (20 ± 1) °C (basic curing – BC), and then either in water (reference medium) and aggressive 5% sodium sulfate solution (33,800 mg SO_3 per liter) for 5-year exposure, respectively.

The tests of chemical resistance were conducted by the own methodology of “partially accelerated tests” [14] based on keeping the mortars in strongly

over-concentrated aggressive solutions for a sufficiently long time. The aggressive environment was specified in the following way: every 1 cm² of the exposed area of prism must be in permanent contact with at least 10 cm³ of 5% wt. Na₂SO₄. A sulfate solution and reference water were refreshed every 30 days within 90 days of testing, every 45 days between 90 and 365 days, and every 60 days up to 5 years of exposure, respectively.

2.3 Testing procedures for cement

All types of cement were tested for chemical composition by STN EN 196–2 [19]; consequently, the Bogue mineral composition was determined. Standard consistency, initial and final set, and soundness were verified by STN EN 196–3 [20]. After 2- and 28-day cure, flexural and compressive strengths of the mortars were obtained according to STN EN 196–1 [21].

2.4 Testing procedures for mortars conducted to sulfate attack

The consistency according to STN EN 1015–3 [22] represents the value of the degree of pouring of the formed fresh mortar after 15 strokes of the compaction table. The bulk density was determined in one-liter container according to STN EN 1015–6 [23]. Based on the consistency results, all mortars fall into the category of plastic mortar, according to STN EN 1015–6. Air content in the mortar was determined by the pressure method according to STN EN 1015–7 [24].

The hardened mortars were during 5 years of sulfate exposure continuously tested for length changes [25], dynamic modulus of elasticity (DME) [26], and periodically for flexural and compressive strength [21]. After destructive tests, the microstructure and pore structure were identified by X-ray diffraction analysis (XRD), thermal analysis (TG-DTA), mercury intrusion porosimetry (MIP), and scanning electron microscopy (SEM) techniques. The grounded mortars were sieved through a 0.063 mm mesh to receive the powder suitable for testing. For the XRD, the Philips diffractometer was used in a 2 Θ range of 5–65°. CuK α radiation and Ni - filter was applied. Thermal analysis was performed on the Netzsch apparatus STA 449 F3 Jupiter in the air at a heating rate of 10°C/min. Basic parameters of the pore structure were identified by MIP using the high-pressure porosimeter Quantachrome Poremaster 60 GT. The JEOL 7500F device was used to study microstructure by scanning electron microscopy. Chemical composition, with special emphasis on the SO₃ content bound in the cement matrix, was estimated by the analytical procedures given in STN EN 196–2 [19].

3. Results and discussion

3.1 Basic properties of cements and mortars after basic curing

Chemical composition of the cements (N – NONRIVAL, SR – sulfate-resistant, and PC – reference Portland) is listed in **Tables 1** and **2**. The content of chloride ions 0.09% wt. in N-cement, 0.07% wt. in SR cement, and 0.06% wt. in PC-cement, is almost the same. The mineral composition was calculated by the Bogue formulas (**Table 2**).

All types of cement meet the requirements for chemical properties, which are given as characteristic values in STN EN 197–1 [4] based on a loss on ignition (LOI), which is less than 5% by weight, an insoluble residue, which is less than 5% by weight, a sulfate content (expressed as SO₃) of less than 4% by weight and a chloride content of less than 0.10% wt.

Cement	LOI (% wt.)	Ins. res. (% wt.)	Content of the component (% wt.)						
			SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Na ₂ O eq.
N	1.9	4.06	19.9	59.9	4.95	3.06	1.3	3.43	1.2
SR	3.5	2.22	21.3	61.0	2.93	4.59	1.6	2.40	0.4
PC	1.6	2.33	17.9	61.5	7.28	2.96	1.9	3.49	0.8

Table 1.
 Chemical composition of the cements.

Cement	Mineral composition (% wt.)			
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
N	44.64	23.64	7.94	9.31
SR	53.36	20.81	0.00	13.97
PC	50.63	13.36	14.28	9.01

Table 2.
 Mineral composition of the cements.

The content of SO₃ in SR cement is less than 3.5% by weight, which meets the additional requirements for sulfate-resistant cement for general use according to STN EN 197–1 [4]. The values of SO₃ content in N- and PC-cement are higher than in SR-cement. In the case of N-cement it is approaching and in the case of PC-cement it reaches the criterion for the maximum SO₃ content in sulfate-resistant cement up to 3.5% by weight. SR-cement is characterized by the highest proportion of calcium silicates (C₃S and C₂S) and tetra calcium aluminat ferrite (C₄AF) compared to N- and PC-cement and C₃A content of 0.00% by weight. Zero C₃A content in SR-cement meets the additional requirement for C₃A content for sulfate-resistant cement of type SR 0 according to STN EN 197–1 [4]. Many C₃S and C₂S phases in SR-cement are an opportunity for the formation of larger amounts of Ca(OH)₂ during hydration, which by its crystalline character markedly affects the formed pore structure and susceptibility to chemical degradation of a cement matrix. N- and PC-cements contain 7.94% wt. and 14.31% wt. C₃A, respectively. Both exceed the requirement for a maximum C₃A content of up to 5% by weight for the type of sulfate-resistant cement CEM I - SR 5 and therefore they cannot be marked as sulfate-resistant types of cement according to the criteria of STN EN 197–1 [4].

The comparison of basic cement properties is reported in **Table 3**. Rheological characteristics of the mortars are presented in **Table 4**. Early- and 28-day strength in basic water curing (BC) is introduced in **Table 5**. N-cement is characterized by the largest specific surface area, normal consistency, flexural and compressive strength values compared to SR- and PC-cement. It is assumed that due to the

Cement	Specific surface area (m ² /kg)	Normal consistency (% wt.)	Initial and final set (min)	Soundness (mm)
N	766.9	35.0	205/270	0.5
SR	354.9	27.2	185/225	1.0
PC	472.4	30.8	265/315	0.0

Table 3.
 Specific surface area and the properties of fresh cement mixtures.

Mortar	Consistency (mm)	Volume density (kg/m ³)	Air content (% vol.)
N	151	2236	4.6
SR	186	2205	6.3
PC	142	2239	4.8

Table 4.
Rheological properties of the fresh mortars.

Mortar	Strength (MPa)			
	compressive		flexural	
	2-day	28-day	2-day	28-day
N	37.1	72.2	7.4	9.2
SR	26.2	52.8	4.7	8.4
PC	31.5	58.0	6.2	8.5

Table 5.
Flexural and compressive strength of the mortars.

higher specific surface area of the N-cement, a denser and therefore less permeable microstructure of the mortar is formed during hydration, as a result of which its sulfate resistance can increase in an aggressive environment.

The normal consistency of the cements represents the water content per amount of cement in the cement paste required to achieve the standardized density [18], expressed in percentage. A higher value of the normal consistency of the N-cement means that a higher amount of water is required to achieve the same density of cement paste than with SR- and PC- cement. The cements meet the criterion for the initial setting according to the requirements of STN EN 197-1 [4] over 60 minutes (strength class 42.5 R) in the case of SR- and PC- cement and over 45 minutes (strength class 52.5 N) in the case of N-cement. The final setting time is not specified by the standard. All types of cement meet the criterion for soundness (volume stability) according to the requirements of STN EN 197-1 [4] that has to be below 10 mm.

The mortars are characterized by different consistency, bulk density, and air content. SR-mortar shows the highest consistency (plasticity 186 mm), lower the N- mortar (151 mm), and the densest was PC mortar (142 mm). In the other words SR- mortar needs less mixing water to achieve the same consistency as N- and PC- mortar. The most probable cause is that the missing tricalcium aluminate (C₃A) phase in SR-cement enables lower binding water consumption to the hydrates of calcium aluminate origin (C-A-H hydrated phase). The rich calcium silicate phase alone is not able to absorb so much water at the beginning of hydration and therefore this cement system is more plastic. This experiment did not deal with adjusting the mortars to the same consistency. The mortars were made with the constant water-to-cement ratio 0.5, and therefore all results are from this viewpoint comparable.

The 28-day volume density, as well as dynamic modulus of elasticity of N-, SR- and PC-mortar, are 2250 kg/m³, 2290 kg/m³, and 2260 kg/m³ as well as 45.3 GPa, 41.8 GPa and 43.1 GPa, respectively. The related strength parameters are reported in **Table 5**.

All cements meet the criteria for minimum compressive strength after 2 and 28 days (initial and standard strengths) according to the requirements of STN EN

197–1 [4]. The mortars with cements of strength class 42.5 R (PC- and SR-mortar) must meet the criteria for compressive strength after 2 days more than 20 MPa and after 28 days more than 42.5 MPa, as required by the STN EN 197–1 [4]. The N-mortar made of high-strength NONRIVAL CEM I 52.5 N meets the strength class of 52.5 N achieving compressive strength after 2 days above 20 MPa and after 28 days above 52.5 MPa. Chemical composition of the mortars after 28 days of basic curing (BC) in the water at $(20 \pm 1)^\circ\text{C}$ is reported in **Table 6**.

The PC-mortar is characterized by the highest, N-mortar by lower, and SR-mortar by the lowest SO_3 content. This finding is in good agreement with the SO_3 content observed in the types of cement (**Table 1**). Changes in the SO_3 contents are one of the important subjects of monitoring the effect of sulfate attack on the mortars over 5-year exposure time. Basic parameters of the pore structure of mortars after BC are listed in **Table 7**. The highest specific surface area of all open pores, the lowest median radius of all pores within the radii range 1.82 nm to 0.534 mm and micro-pores between 1.82 nm to 5.25 μm points for the presence of the largest share of micro-pores in N-mortar compared to SR- and PC-mortar. This fact is reflected in the formation of a denser, less permeable pore structure of N-mortar also characterized by the lowest total pore volume, total porosity, and the lower permeability coefficient by one order of magnitude compared to SR- and PC-mortar.

The mineral composition of individual cement types together with their fineness generally influences the microstructure formation during hydration, from which depends the condition of the developed pore structure of mortars. The character of the pore structure subsequently determines the permeability of the mortar against the penetration of sulfate solution into the internal structure. The impermeable pore structure is one of the important properties of the cement matrix in terms of environmental resistance.

Explanatory notes to the **Table 7**: specific surface area of all measured pores - SSA, total pore volume - VTP in the measured range of porosimeter 1,82 nm - 0,534 mm, the median radius of micro-pores in the range of 1,82 nm - 5,25 μm , that of macro-pores between 5,25 μm - 0,534 mm and total pores within pore radii of

Mortar	Ign. loss (% wt.)	Content of the component (% wt.)							
		SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	Cl ⁻	Na ₂ O eq.
N	7,93	73.08	15.28	0.95	1.14	0.38	0.82	0.03	0.15
SR	8,45	68.99	18.43	0.91	1.80	0.55	0.69	0.02	0.07
PC	7,59	70.99	16.69	1.23	1.14	1.04	0.92	0.02	0.13

Table 6.
 28-day chemical composition of the mortars.

Mortar	SSA (m ² /g)	VTP (cm ³ /g)	Pore median of			TP (%)	CP (m/s)
			total pores (nm)	micro-pores (nm)	macro-pores (nm)		
N	6.93	0.070	40.10	30.80	9.30	13.70	7.0×10^{-11}
SR	4.02	0.077	67.90	43.21	24.69	16.20	3.0×10^{-10}
PC	4.85	0.079	59.99	42.24	17.75	14.92	2.0×10^{-10}

Table 7.
 Pore structure parameters of the mortars after 28-day basic curing.

1,82 nm - 0,534 mm, total porosity TP estimated among pore radii between 1,82 nm - 0,534 mm and calculated coefficient of permeability CP for water valid within the scope of porosimetry measurements.

3.2 Partially accelerated sulfate resistance test

After 28-day BC in the water at $(20 \pm 1) ^\circ\text{C}$ when the mortars reached naturally developed physical-mechanical properties, microstructure, and pore structure, one-half of the mortars were immersed in 5% sodium sulfate solution and the second half of the specimens was still left in the reference water. The partially accelerated test of sulfate resistance of cement mortar is based on long-term, usually two-year, but in this case, even five-year monitoring of a) changes of physical and mechanical properties by non-destructive and destructive testing and b) changes of microstructure and pore structure in 5% sodium sulfate. The obtained results from the sulfate exposure were compared to each other according to the type of cement as well as with those coming from the reference water.

3.2.1 Changes in physical and mechanical properties

Figure 1 shows the changes in dynamic modulus of elasticity (DME) of different mortars (N – NONRIVAL CEM I 52.5 N, SR - sulfate-resistant, and PC – Portland cement) during 5-year exposure in aggressive 5% Na_2SO_4 solution and reference water after 28 days BC. **Figure 2** presents the percentage decrease in the DME of N-, SR- and PC-mortar in the sodium sulfate compared to the reference water.

The N-mortar and SR-mortar show comparable DME changes, while the PC-mortar is subject to the harmful effect of aggressive sulfate attack.

The length changes of mortars during the 28-day BC and 5-year exposure in 5% Na_2SO_4 and water are illustrated in **Figure 3**. The PC-mortar expands significantly during 5 years of exposure in sulfate up to the level of 18.131 mm/m. This expansion gives evidence of the aggressive action of sodium sulfate. Visual observations of the

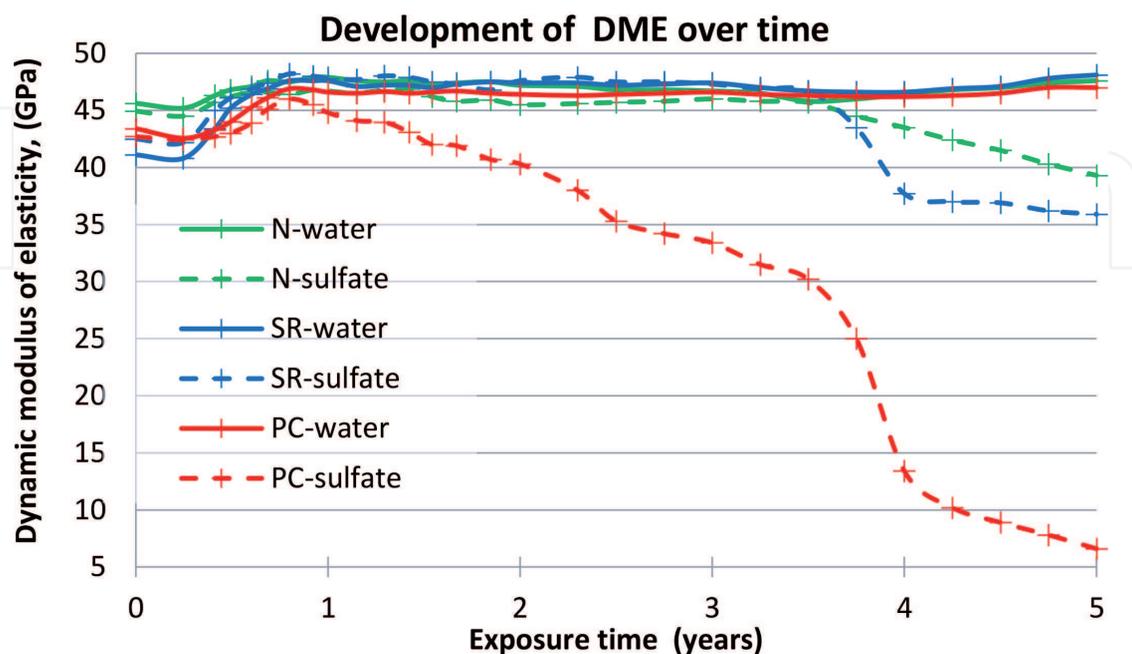


Figure 1. Changes in dynamic modulus of elasticity of the mortars over time.

Comparison of the percentage losses in DME

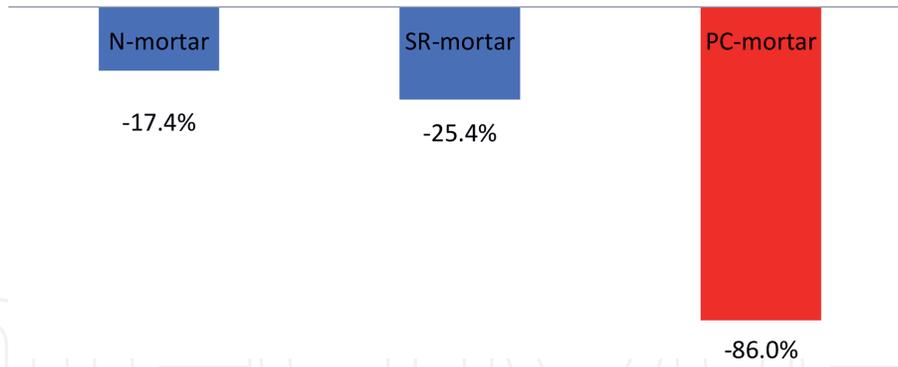


Figure 2. Percentage loss of dynamic modulus of elasticity of N-, SR- and PC-mortar after 5-year exposure in sodium sulfate compared to the reference water.

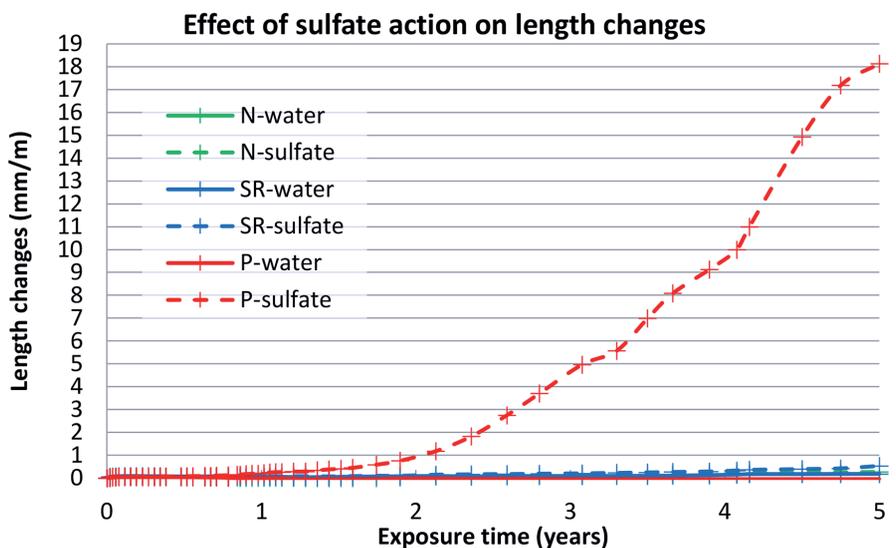


Figure 3. Length changes of the mortars over time.

PC-mortar show the cracks on the surface of the test prisms, which propagate into the mortar interior over the time. The cracks were mainly observed in the rounding of the prism corners by the loss of the peeled cement matrix. This fact is confirmed by the photo in **Figure 4**.

Figure 5 shows the decrease in compressive strength of all mortars stored in sulfate for 5 years compared to reference water. The largest strength loss is recorded in PC-mortar.

The changes in flexural strength of SR- and N-mortar exposed for 5 years in sulfate are negligible (**Figure 6**). The PC-mortar immersed for the same time in aggressive solution significantly loses the flexural strength to a critical value of 2.8 MPa from 9.6 MPa in water storage. The related loss of flexural strength of PC-mortar is 70.8% wt. (**Figure 6**).

The evaluation of the strength characteristics results in the following partial findings: while N- and SR-mortar show similar sulfate resistance, the apparent strength losses of PC-mortar confirm the well-known evidence that Portland cement is unsuitable for use in a sulfate environment. N-mortar still reaches a sufficiently high strength after 5 years of sulfate attack.



Figure 4.
View on the disturbed surface of PC-mortar exposed for 5 years in 5% sodium sulfate solution.

Percentage loss in compressive strength between sulfate and water storage



Figure 5.
Percentage loss in compressive strength of N-, SR- and PC-mortar after 5- year exposure in sodium sulfate compared to the reference water.

3.2.2 Changes in microstructure and pore structure

Changes in the physical and mechanical properties of mortars during long-term water and sulfate exposure are a reflection of the formed microstructure and developed pore structure, which mainly depend on the composition and properties of the used types of cement. The mortar's microstructure was studied every year till the end of the experiment by a XRD, thermal and chemical analysis. After 5-year sulfate exposure, the pore structure was identified by MIP and the microstructure observed by the SEM technique. These results serve to elucidate the mechanism of sulfate resistance with special regard to revealing a nature of the sulfate resistance

Percentage changes in flexural strength
 between sulphate and water storage

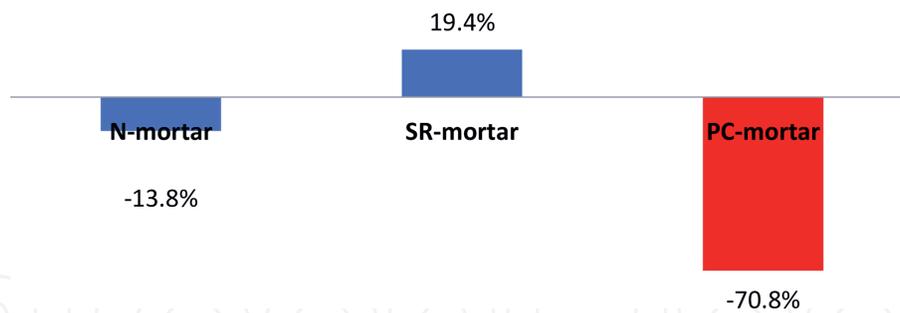


Figure 6.
 Percentage changes in flexural strength of N-, SR- and PC mortar after 5-year exposure in sodium sulfate solution compared to the reference water.

of N-mortar. This section presents 5-year results that have made a decisive contribution to clarifying the mechanism of sulfate resistance of NONRIVAL CEM I 52.5 N that is explained in Section 4.

3.2.2.1 X-ray diffraction analysis

XRD analysis determines the qualitative portion of minerals, from which it is not possible to quantify their content, but a comparison of intensity and number of diffractions gives an approximate picture of the mineral content in the mortars. The presence of gypsum (G) and/or ettringite (E) is a decisive indicator of sulfate attack. A comparison of X-ray records of N-mortar after 5 years of exposure in water and 5% Na₂SO₄ is illustrated in **Figure 7**.

Comparison of X-ray records of SR-mortar and PC-mortar after 5 years of exposure in water and 5% Na₂SO₄ is given in **Figures 8** and **9**, respectively.

After 5 years of exposure to sodium sulfate, the PC-mortar shows a high proportion of the formed gypsum (G: CaSO₄·2H₂O) as well as also ettringite (E: 3CaO·Al₂O₃·3CaSO₄·32H₂O) as reaction products of the sulfate attack.

Figure 10 confirms that SR- and N- mortar are characterized by a negligible amount of G and E. Besides these products, every mortar contains portlandite [CH: Ca(OH)₂] and quartz coming from a standard sand Q: SiO₂.

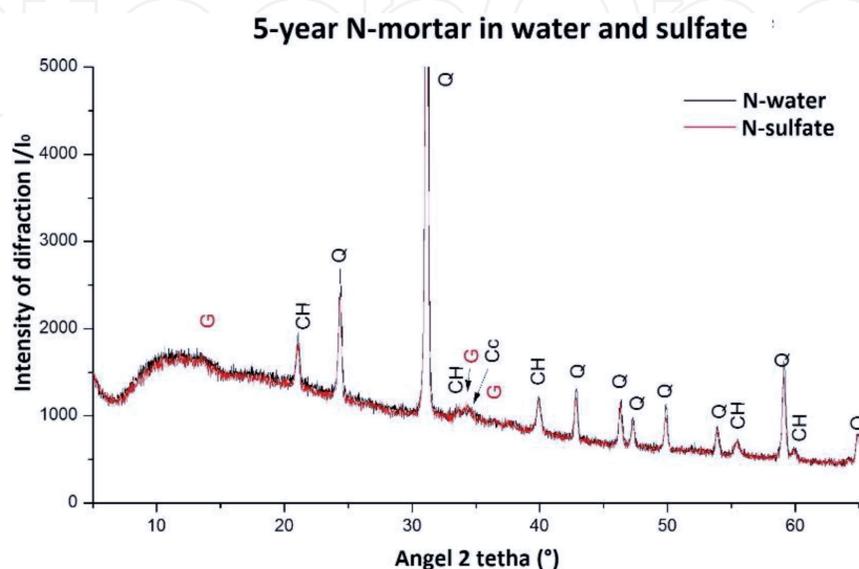


Figure 7.
 Mineral composition of 5-year N-mortar in water and sulfate.

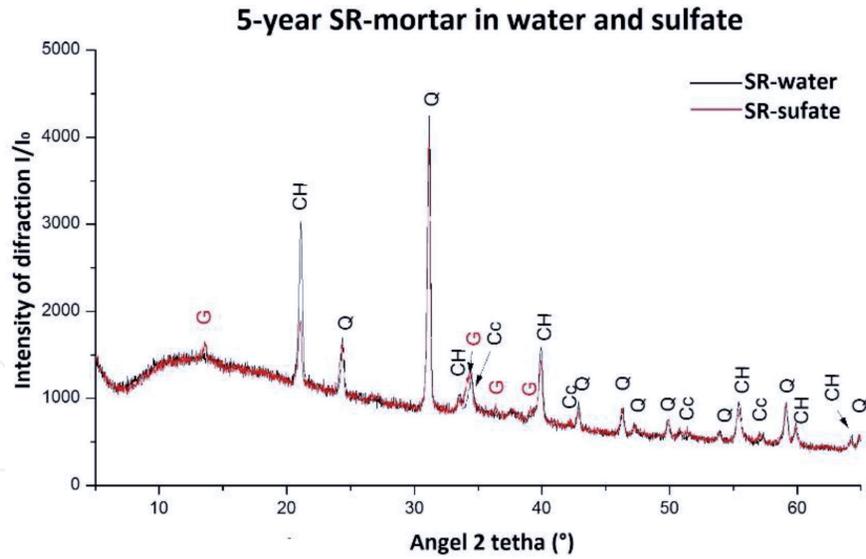


Figure 8.
Mineral composition of 5-year SR-mortar in water and sulfate.

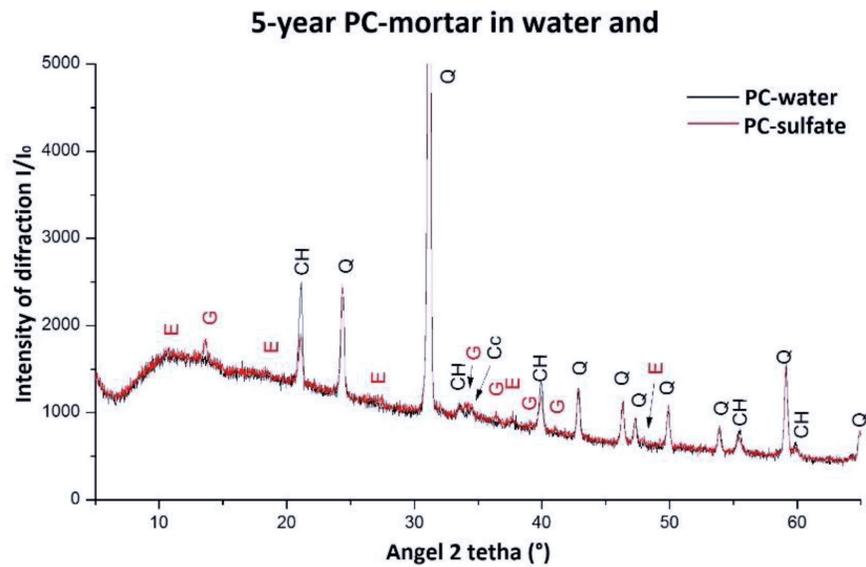


Figure 9.
Mineral composition of 5-year PC-mortar in water and sulfate.

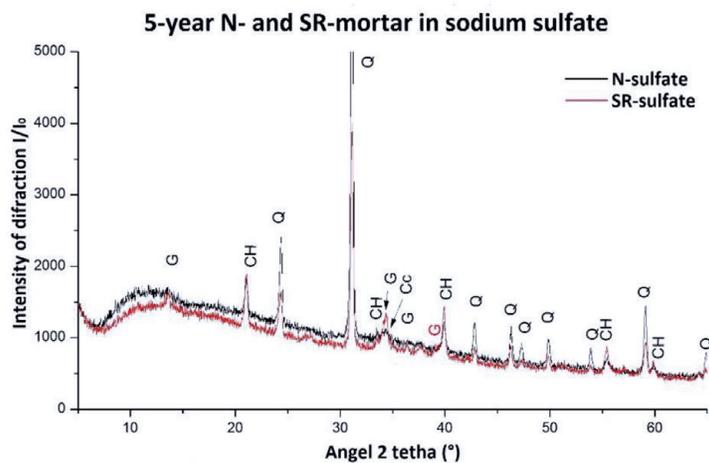


Figure 10.
Comparison of X-diffraction patterns of 5-year N- and SR-mortar from sodium sulfate.

3.2.2.2 Thermal analysis

Thermal analysis (TG-DTA) qualitatively and quantitatively determines the proportion of cement hydration products and products of sulfate attack in the mortars based on the observed mass losses and the relevant endotherms in the respective temperature ranges. The dissociation energy provides information on the incorporation strength of individual releasable components identified by the XRD technique.

The results of the thermal analysis of the 5-year mortars are shown in **Figures 11–13**. The percentage values of present phases and related dissociation energies are reported in **Table 8**. According to **Table 8**, the N-mortar in water contains the lowest proportion of portlandite - $\text{Ca}(\text{OH})_2$. All mortars show a decrease in portlandite content after 5 years of exposure to sodium sulfate compared to water. The lowest 0.29% wt. loss is observed in the N-mortar. PC-mortar is characterized by portlandite decrease 3.25% wt. and SR-mortar 4.93% wt. The difference in energy required for the endothermic reaction in the temperature range of 100–200°C in sulfate solution and water can be taken as a measure of gypsum and ettringite incorporation in the mortar's microstructure. The energy value for N-mortar is 3.05 J/mg, for SR-mortar 13.92 J/mg and for PC-mortar 22.83 J/mg. The quantitative representation of G and E as the

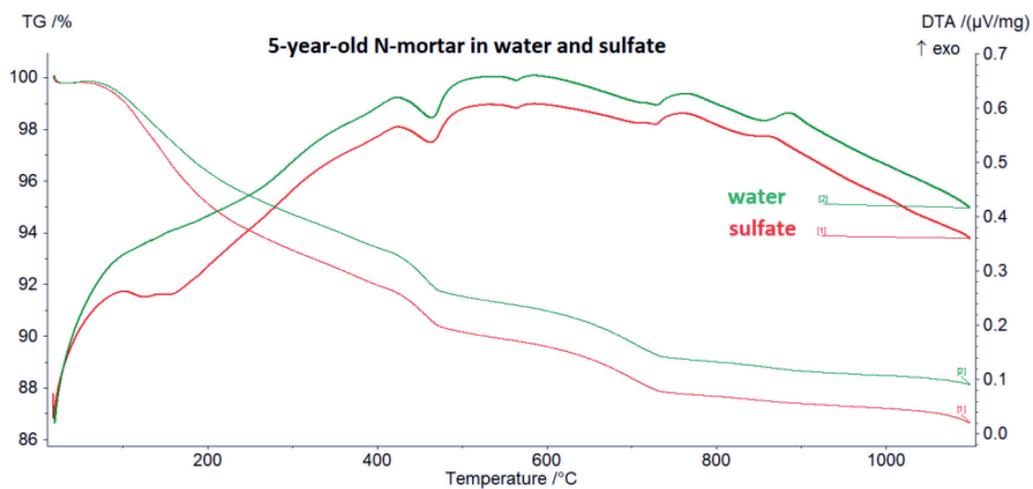


Figure 11.
Comparison of TG-DTA plots of 5-year-old N-mortar in water and sulfate.

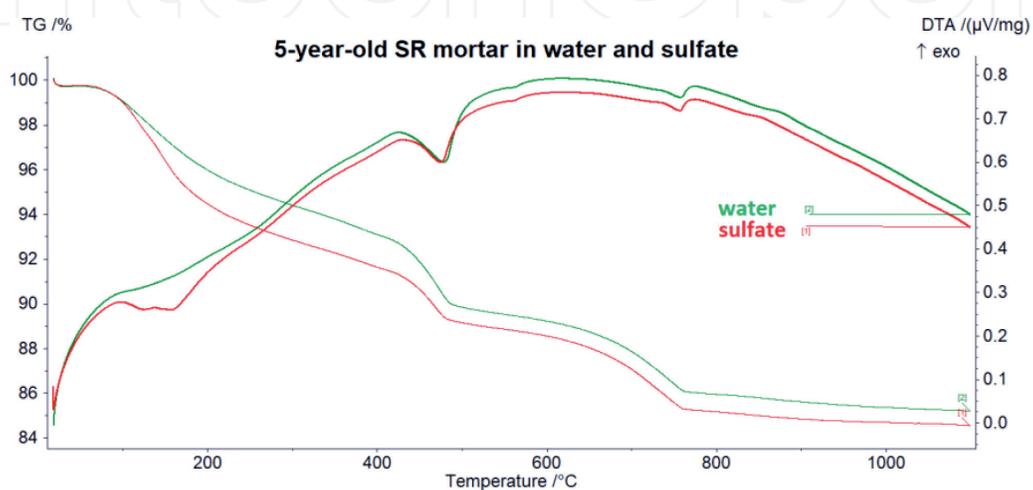


Figure 12.
Comparison of TG-DTA plots of 5-year-old SR-mortar in water and sulfate.

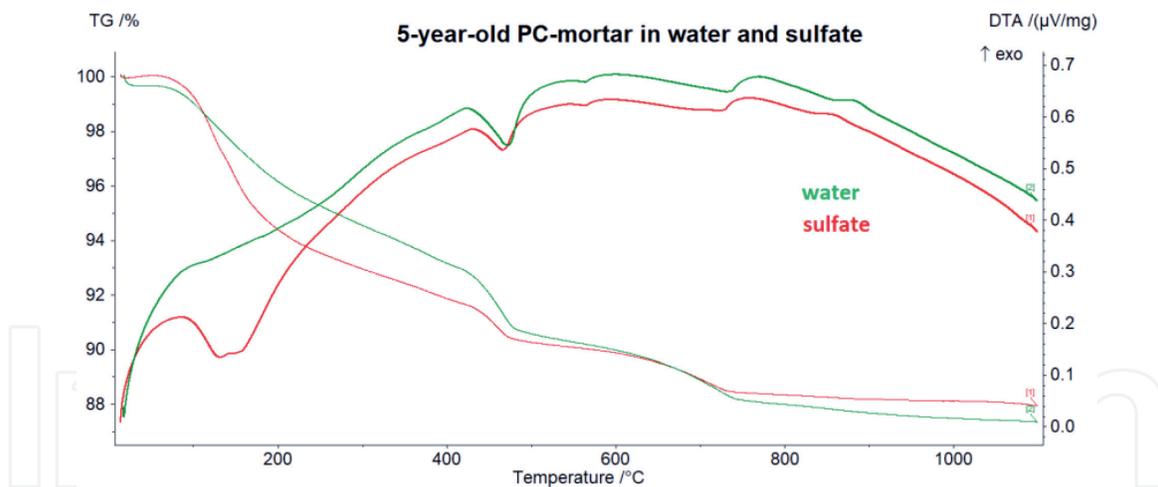


Figure 13.
Comparison of TG-DTA plots of 5-year-old PC-mortar in water and sulfate.

Mortar	Total ignition loss between (20–1100) °C (% wt.)	Content of		Loss in Ca(OH) ₂ in sulfate (% wt.)	Dissociation energy between (100–200) °C (J/mg)	Energy difference between (100–200) °C (J/mg)
		Ca(OH) ₂ (% wt.)	Ca(CO) ₃ (% wt.)			
N-water	11.86	10.03	6.46	0.29	0.00	3.05
N-sulfate	13.35	9.74	6.71		3.05	
SR-water	14.85	15.91	9.14	3.25	0.00	13.92
SR-sulfate	15.44	12.66	9.1		13.92	
PC-water	12.64	13.07	5.98	4.93	0.00	22.83
PC-sulfate	12.06	8.14	4.43		22.83	

Table 8.
Phase composition of the mortars after 5 years of exposure in 5% sodium sulfate solution and reference water at (20 ± 1) °C.

products of sulfate attack is in N-mortar and SR-mortar equally marginal and even the same. On the contrary, PC-mortar shows at the same time the evident presence of gypsum and ettringite.

PC-mortar contains the most quantum of reaction products of the sulfate attack compared to SR- and N-mortar as previously approved by the X-ray analysis. TG-DTA data indicate the equally high sulfate resistance of the N- and SR-mortar.

3.2.2.3 Chemical analysis

The chemical analysis was used to compare the oxide content in mortars with a focus mainly on the SO₃ content. The analysis of the chemical composition does not unambiguously determine the proportion of sulfate attack reaction products but a comparison of the SO₃ content bound in these reaction products gives a picture of the intensity of the acting sulfate aggressiveness. The increase in SO₃ content in the mortar is due to the penetration of sulfate ions from the solution into the internal matrix and the transformation of calcium hydroxide and/or calcium silicate hydrate resp. calcium aluminate hydrate (C-S-H/C-A-H) to CaSO₄·2H₂O and 3CaO·Al₂O₃·3CaSO₄·32H₂O [1–3]. A typical symptom of sulfate attack of cement mortar is an increased SO₃ content, which announces the presence of gypsum and ettringite.

This fact is confirmed by the increase of SO_3 in the mortars during 5 years of exposure to 5% Na_2SO_4 (**Figure 14**). The content of SO_3 is in the N-, SR- and PC-mortar after 28-day BC was 0.82%, 0.69% and 0.92% wt., respectively. The 5-year exposure records an increase in the bound SO_3 content to the value of 3.60% wt. in N-mortar, 3.75% wt. in SR-mortar and 6.20% wt. in PC-mortar, while the content of SO_3 in 5-year water storage is 1.54% wt. for N-mortar, 1.31% wt. for SR-mortar and 1.65% wt. for PC-mortar.

The chemical composition of the studied mortars with the attention focused on the typical symptom of sulfate attack - the SO_3 content - shows that N- and SR- mortar after 5-year exposure in 5% Na_2SO_4 are equally characterized by a slight increase in the bound SO_3 content. In contrast, PC-mortar shows at the same time an evident increase of SO_3 . Bearing in mind the previous findings of XRD and thermal analysis, chemical analysis points to the fact that the sulfate resistance of the N- and SR-mortar is very similar, even the same, and that both types of cement could be, from this point of view, fully comparable.

3.2.2.4 Pore structure

Basic pore structure parameters after 5 years of exposure to water and sulfate are listed in **Table 9**. The knowledge gained so far suggests that the reaction products (gypsum -G and ettringite -E) are formed during a sulfate attack, which first densifies the pore system. After depletion of the pore storage space by the voluminous G and E reaction products, a loss in the integrity of the formed microstructure starts to occur. In the advanced stage of the sulfate attack when there is observed a loss in mechanical properties and intense expansion, the mortar is characterized by the pore structure coarsening, in particular by the increased porosity. The increased porosity leads to the easier permeability of aggressive sulfate into the internal mortar body. The most evident indicators of these manifestations are the changes in the total pore median radius and total porosity. Changes in basic parameters of the pore structure have therefore a significant impact on the increased permeability.

N-mortar, regardless of the exposure either in water and or the aggressive sulfate, shows in the time horizon of the experiment only a slight pore structure coarsening

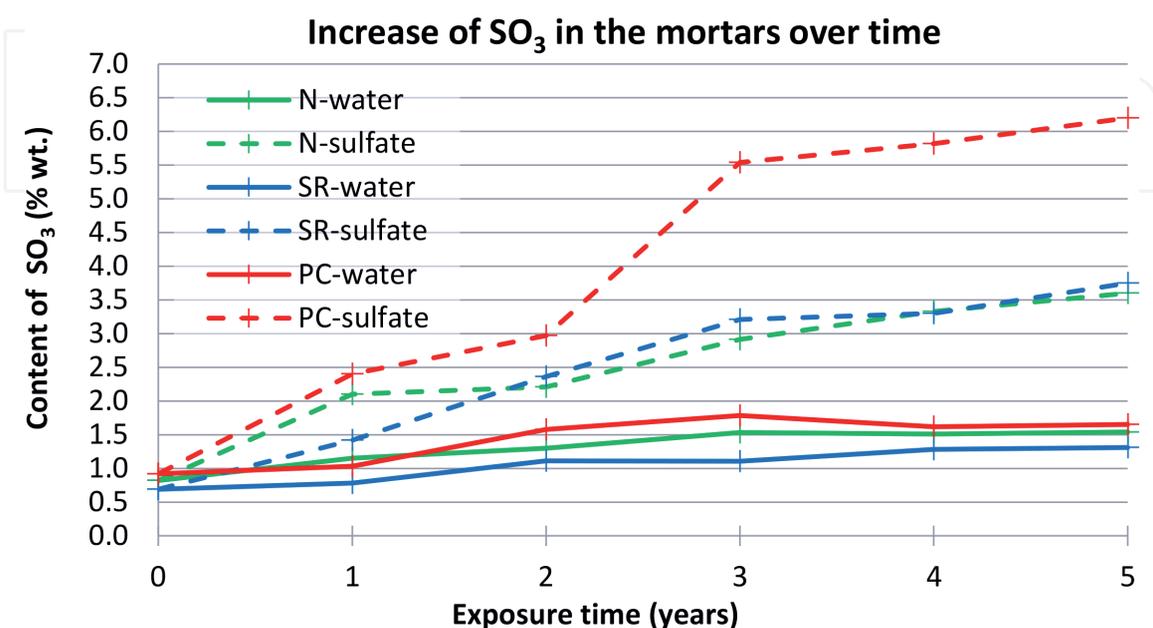


Figure 14. Changes in SO_3 content in N-, SR- and PC-mortar immersed for 5 years in water and sodium sulfate after 28 days of basic curing in water.

Mortar	SPA (m ² /g)	TPV (cm ³ /g)	Pore median radius		TP (%)	CP (m/s)
			of total pores (nm)	of micro-pores (nm)		
N-water	7.10	0.072	33.52	25.76	15.41	2.0 × 10 ⁻¹¹
N-sulfate	5.41	0.070	38.84	26.72	14.32	1.2 × 10 ⁻¹¹
SR-water	6.02	0.071	64.95	35.92	14.95	8.0 × 10 ⁻¹¹
SR-sulfate	5.90	0.065	65.40	28.51	13.49	7.0 × 10 ⁻¹¹
PC-water	6.86	0.072	37.84	25.16	15.25	3.0 × 10 ⁻¹¹
PC-sulfate	5.71	0.083	292.0	2.98	17.03	1.6 × 10 ⁻¹⁰

Explanatory notes – the same as for Table 7.

Table 9.

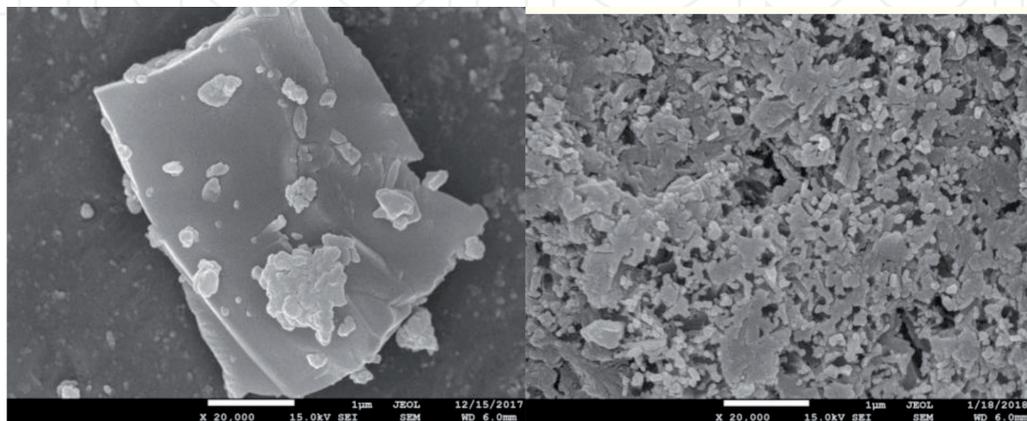
Comparison of basic parameters of the pore structure of 5-year mortars.

demonstrated by 1) slight decrease in the specific surface area of the measured pores, 2) slight decrease in the total pore volume, 3) a slight increase in the total pore and micro-pore median radii, 4) slight decrease in total porosity in the range of porosimeter measurements and 5) at unchanged permeability at the level of 10⁻¹¹.

The permeability of the 5-year N-mortar kept in an aggressive sulfate solution is very close to the permeability of the mortar cured for the same time in the water. The reference SR-mortar shows very similar behavior as the N-mortar. The pore structure is not significantly influenced by the sulfate attack. By contrast with it, the PC-mortar is characterized by the typical consequences of sulfate attack proved mainly by an obvious increase in total pore median radius in the aggressive sulfate and the increase in permeability by one order of magnitude to 10⁻¹⁰ m/s compared to reference water curing.

3.2.2.5 Scanning electron microscopy

The SEM visually identifies differences in the mortar microstructure between sulfate and water storage. Gypsum crystals have various shapes, most often acicular, prismatic or lenticular, while ettringite crystals are very thin and needle-like. The SEM images of N-mortar are shown in **Figure 15**, while those of PC-mortar in **Figure 16**. The SEM confirms the presence of crystalline Ca(OH)₂ in water as

**Figure 15.**

SEM image of N-mortar after 5-year exposure to water (left) and 5% solution of Na₂SO₄ (right) (magnification 20,000 ×).

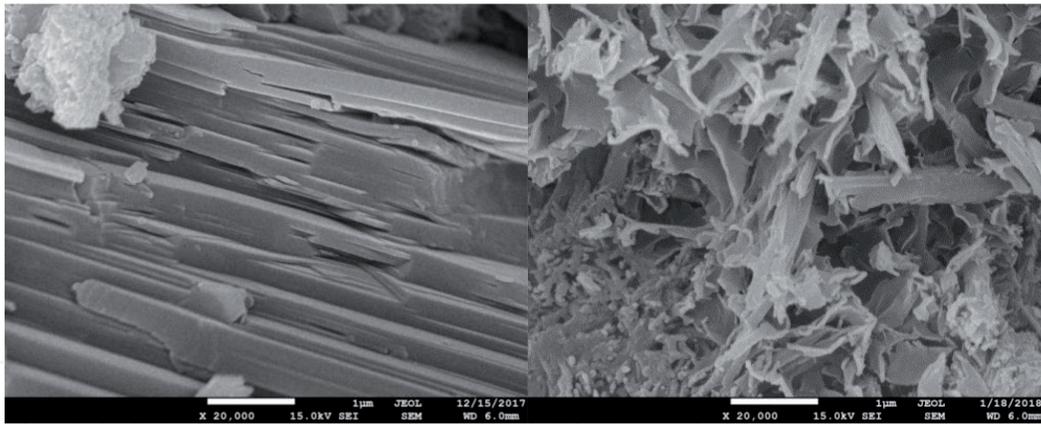


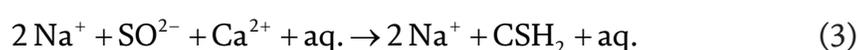
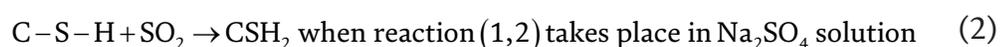
Figure 16. SEM image of PC-mortar after 5-year exposure to water (left) and 5% solution of Na_2SO_4 (right) (magnification 20,000 ×).

well as the presence of gel hydration products of the C-S-H and C-A-H type with minimal occurrence of calcite, also taking into account differences depending on the type of cement. After 5 years of exposure to sodium sulfate, N-mortar records a negligible presence of rod-shaped crystallites (**Figure 15**), while the proportion of these reaction products, which most likely belong to gypsum and ettringite, is dominant in PC-mortar (**Figure 16**).

Summarization of the knowledge according to evaluation of the formed microstructure (XRD, TG-DTA, chemical analysis, SEM) and pore structure (MIP) of the mortars after 5 years of exposure is:

1. the N-mortar made with NONRIVAL CEM I 52.5 N is characterized by the same resistance to the aggressive sodium sulfate in terms of maintaining mechanical properties and structural integrity as the reference SR-mortar made with sulfate-resistant cement of none C_3A content;
 2. NONRIVAL CEM I 52.5 N, therefore, declares the same sulfate resistance as the sulfate-resistant CEM I 42.5 R – SR;
 3. PC-mortar shows disrupted structural integrity and confirms the well-known fact that ordinary Portland CEM I 42.5 R is not resistant to sulfate aggressiveness.
- 4. Explanation of the cause of sulfate resistance of NONRIVAL CEM I 52.5 N**

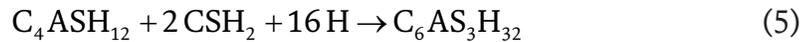
Degradation of the hydrated phase of the cement matrix by aggressive sulfate is characterized by the formation of gypsum $\text{CaSO}_4 \times 2 \text{H}_2\text{O}$ (CSH_2) together with ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ ($\text{C}_6\text{AS}_3\text{H}_{32}$). Gypsum is formed by the reaction of sulfate ions with calcium hydroxide $\text{Ca}(\text{OH})_2$ or with calcium silicate hydrate (C-S-H).



The formed gypsum binds with tricalcium aluminate (C_3A) mainly to ettringite but monosulfate C_4ASH_{12} is also secondarily present.



Ettringite formation is accompanied by another minor reaction.



The damage mechanism is defined by gypsum and ettringite formation as the reaction products of aggressive sulfate action, being formed as high bulk, voluminous salts that cause destructive expansion of a cement stone. In the reaction 1 and 3, respectively active submicron-sized pozzolan present in NONRIVAL CEM I 52.5 N binds CaO from a supersaturated solution of $Ca^{2+} OH^-$ by the pozzolanic reaction so that the formation of $Ca(OH)_2$ and thus gypsum CSH_2 is extensively eliminated.

Such limited $Ca(OH)_2$ formation due to the pozzolanic reaction of submicron-sized addition subsequently prevents an excessive formation of generated gypsum, required for the ettringite development. The markedly reduced formation of $Ca(OH)_2$ required for the reaction with sulfate ions (see Eq. 1) is the basic condition for suppressing the aggressive effect of sulfate solution on the NONRIVAL CEM I 52.5 N - containing mortar. This is regarded as a new effective reaction mechanism leading in the final effect to the increased sulfate resistance of NONRIVAL CEM I 52.5 N to the same level as that of a sulfate-resistant cement with none of C_3A .

Sulfate-resistant cement (SR) is characterized by blocking gypsum formation and subsequent ettringite due to the absence of C_3A , while NONRIVAL CEM 52.5 N blocks the formation of these reaction products by minimizing the $Ca(OH)_2$ content by the presence of active submicron-based pozzolan. Both alternatives to preventing sulfate aggression mitigate the formation of CSH_2 to a harmless content level but in a different way.

5. Conclusions

Five-year tests of the mortars in 5% sodium sulfate solution show the following key conclusions:

Sulfate resistance of cement NONRIVAL CEM I 52.5 N is the same as sulfate-resistant cement CEM I 42.5 R - SR. The cause lies in the thorough elimination of $Ca(OH)_2$ formation by the active submicron-based pozzolanic addition. The formation of gypsum and ettringite is therefore extensively minimized to harmless content. Reference CEM I 42.5 R does not confirm the resistance to the sulfate solution. For the needs of construction practice, NONRIVAL CEM I 52.5 N represents an equivalent alternative to the use of sulfate-resistant cement in terms of resistance to sulfate aggression.

Other crucial findings coming from the 5-year experiment are:

NONRIVAL CEM I 52.5 N can be advantageously applied in technically demanding structural concrete, in which high strength but at the same time low permeability of the concrete foundation slab is required as a basic condition for ensuring its durability when exposed to aggressive sulfate for a long time. High strength and low penetration permeability are two equally important conditions for achieving a high durability.

Further research should focus on verifying a long-term performance of NONRIVAL CEM I 52.5 N in other aggressive environments.

The recommendation beyond domestic research is:

The development of the unified method, at the best standardized in EN or ASTM, even one common, for the evaluation of concrete's resistance to sulfate attack by an accelerated testing procedure, is required.

Equally urgent scientific task is the most accurate transformation of the accelerated test results to a realistic estimation of concrete service-life when subjected to natural aggressiveness e. g. related to the XA (1–3) exposure classes of STN EN 206 + A1.

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Conflict of interest

The authors declare no conflict of interest.

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