Corrosion Resistance of Ordinary and Special Portland Cements in the Sulfate and Chloride Environments

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1. Introduction

HSR and MSR sulfate resistant cements are widely used in communication constructions. Such constructions are submitted to various external conditions, including sulfates and, as well, deicing salts. The base form of chloride ion bonding is their reaction with C_3A. As a result calcium aluminum chloride, known as Friedel's salt is generated [1]. In similar reactions with C_4AF chloride ferrite is generated. This problem is interesting for scientists[2], because cements from HSR and MSR group, providing high resistance to sulfate environments, are of low C_3A contents [3,4].

The problem discussed in this article is: to what extent the cements, providing high sulfate resistance, can be as well resistant to chloride environments, created by the use of deicing salts on roads and bridges.

2. Cements characteristics and the research range

In the research sulfate resistant cements CEM I 42,5 HSR NA and CEM I 42,5 MSR NA and ordinary Portland cement CEM I 42,5 NA were used. The characteristics of the cements are shown in Table 1.

In order to state the mechanical and vulnerability to sulfate and chloride environments control beams with dimensions of 0,04×0,04×0,16 m were produced of cements and standard sand.

As aggressive environments the following agents were used:

- Na_2SO_4 solution, containing sulfate ions (3750 mg),
- one mole NaCl solution, which corresponds to the concentration of evenly distributed deicing salt solution (5.8% solution),
- four mole NaCl solution (23.5% solution), which corresponds to the characteristic assemblies of deicing salt, which are left in the surface asperities

Table 1

The characteristics of CEM I 42,5 NA, CEM I 42,5 MSR NA and CEM I 42,5 HSR NA cements

No.	Characteristics	CEM I 42,5 NA	CEM I 42,5 MSR	CEM I 42,5 HSR
1	Chemical composition [%]			
	loss by roasting	1,02	0,70	0,50
	insoluble components	0,60	0,50	0,30
	CaO	65,20	64,80	64,80
	SiO_2	22,10	21,30	21,20
	Al_2O_3	4,80	4,30	4,10
	Fe_2O_3.	2,17	3,60	4,80
	MgO	2,35	0,90	0,90
	SO_3	3,17	2,60	2,40
	Cl^-	0,005	0,006	0,004
	Alcalies (as Na_2Oeq)	0,82	0,45	0,45
2	Physical characteristics			
	Proper surface (cm^2/g)	3500	3100	3000
	time of bonding (min)			
	the beginning	135	200	210
	the end	210	300	310
3	clinker phase composition [%]			
	C_3A	9,1	5,30	2,73
	C_4AF	6,6	10,94	14,59
	C_3S	64,8	56,65	58,80
	C_2S	12,0	18,31	16,40

The rating of the mechanic characteristics of the cements was carried out using the comparative method, i.e. each of the examined cements was compared to ordinary Portland cement CEM I 42,5 NA.

The samples were placed in water or aggressive, sulfate and chloride environments.

The aggressive impact was examined after 1, 3, 6, 12, 18, 24 and 36 months since the samples were placed in the environment.
For comparison of the results obtained the corrosion resistance rate was stated, following the formula:

$$CR = \frac{f_{c.aggres.env.}}{f_{cH_2O}}$$

where:

CR	-	corrosion resistance rate,
$f_{c\ aggres.env.}$	-	bend strength of the samples kept in aggressive environment,
f_{cH_20}	-	bend strength of the samples kept in comparative water environment

Cements with higher resistance is cement, for which CR $\geq$ 0.75.

Due to the limits to the article the most characteristic research results of the mechanical characteristics were chosen.

The next stage of the research were a microscopic and x-ray structural tests showing the characteristics of the cements, which have been submitted to sulphate and chloride environments impact.

For the microstructure rating the VEGA TS 5135 MM scanning microscope with low vacuum 10Pa was used. The x-ray tests on powder specimens were conducted at two subranges of angles $2\theta \rightarrow 4°\text{-}10°$ and $2\theta \rightarrow 10°\text{-}80°$. The results are presented below.

3. The mechanical characteristics rating – corrosion resistance rate

The corrosion resistance rates during the test beams bending are presented in Tables 2, 3 and 4.

Table 2

The corrosion resistance rates CR of the bending strength of the examined cements, which have undergone the aggressive environment impact of SO_4^{-2} with 3750 mg/l concentration after 1, 3, 6, 12, 18, 24 and 36 months of the impact

Type of cement	Corrosion resistance rate CR after:						
	1 m.	3m.	6 m.	12 m.	18 m.	24 m.	36 m
Portland cement CEM I 42,5 NA	1,064	0,994	1,024	1,223	0,976	0,912	0,643
CEM I 42,5 MSR NA	1,082	0,955	0,942	0,940	0,890	0,800	0,744
CEM I 42,5 HSR NA	1,255	1,176	1,070	1,046	0,954	0,938	0,751

Table 3

The corrosion resistance rates CR of the bending strength of the examined cements, which have undergone the aggressive environment impact of 1-mole chloride solution after 1, 3, 6, 12, 18, 24 and 36 months of the impact

Type of cement	Corrosion resistance rate CR after:						
	1 m.	3m.	6 m.	12 m.	18 m.	24 m.	36 m
Portland cement CEM I 42,5 NA	1,107	1,044	1,061	0,947	0,926	0,797	0,656
CEM I 42,5 MSR NA	1,119	0,928	0,896	0,884	0,882	0,847	0,722
CEM I 42,5 HSR NA	1,075	1,048	1,017	1,001	0,955	0,827	0,705

Table 4

The corrosion resistance rates CR of the bending strength of the examined cements, which have undergone the aggressive environment impact of 4-mole chloride solution after 1, 3, 6, 12, 18, 24 and 36 months of the impact

Type of cement	Corrosion resistance rate CR after:						
	1 m.	3m.	6 m.	12 m.	18 m.	24 m.	36 m
Cement portlandzki CEM I 42,5 NA	1,024	1,155	1,075	0,890	0,745	0,713	0,523
Cement CEM I 42,5 MSR NA	1,283	1,040	0,808	0,783	0,775	0,746	0,541
Cement CEM I 42,5 HSR NA	1,287	1,416	1,044	0,825	0,781	0,756	0,561

The results of the research presented above show the differences in the chemical reaction process between the hydrates of the examined cements and the components of the aggressive environments. The phenomena of sealing the cement stone and its decomposition appear in different terms and the range of them also varies.

4. Microscopic and x-ray structural tests

For the samples made of analyzed cements after the 36 months impact of aggressive environments, microscopic and x-ray structural tests were conducted. The microscopic pictures are presented in Figures 1, 2, 3 and 4.

Fig. 1. Microscopic pictures of the mortars stored in comparative water environment – the differences in the structure are visible:
1 – mortar made from Portland cement CEM I 42,5, 2 – mortar made from cement CEM I 42,5 MSR NA, 3 – mortar made from cement CEM I 42,5 HSR NA

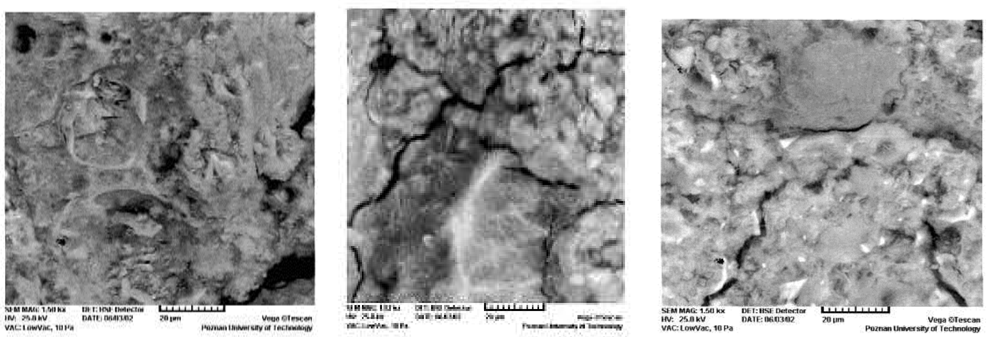

Fig. 2. Microscopic pictures of the mortars stored in aggressive sulfate environment – the differences in the structure are visible:
1 – mortar made from Portland cement CEM I 42,5, 2 – mortar made from cement CEM I 42,5 MSR NA, 3 – mortar made from cement CEM I 42,5 HSR NA

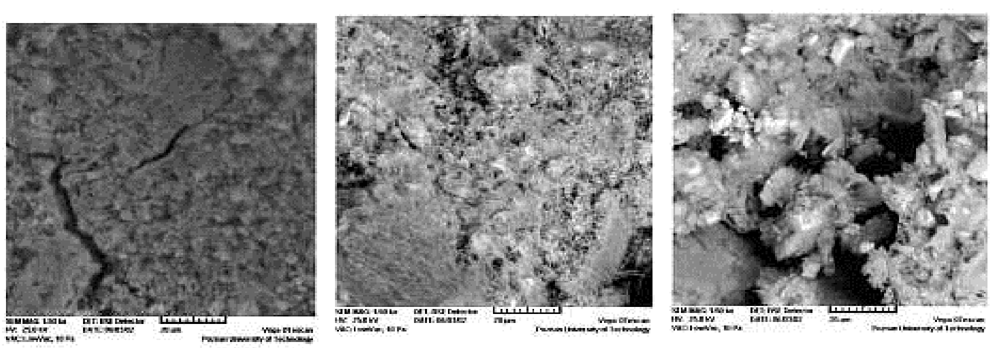

Fig. 3. Microscopic pictures of the mortars stored in aggressive 1-mole chloride environment – the differences in the structure are visible:
1 – mortar made from Portland cement CEM I 42,5, 2 – mortar made from cement CEM I 42,5 MSR NA, 3 – mortar made from cement CEM I 42,5 HSR NA

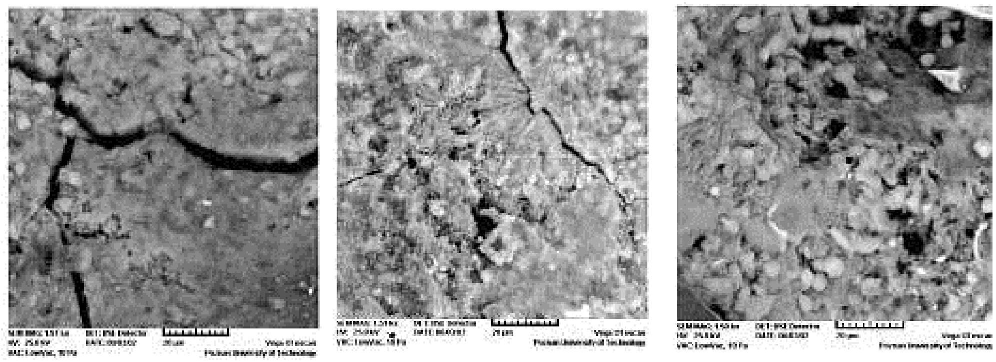

Fig. 4. Microscopic pictures of the mortars stored in aggressive 4-mole chloride environment – the differences in the structure are visible: 1 – mortar made from Portland cement CEM I 42,5, 2 – mortar made from cement CEM I 42,5 MSR NA, 3 – mortar made from cement CEM I 42,5 HSR NA.

The x-ray tests were conducted at two subranges of angles $2\theta \rightarrow 4°-10°$ and $2\theta \rightarrow 10°-80°$.

The results of the research were dyfractograms, one of which is shown in Fig. 5.

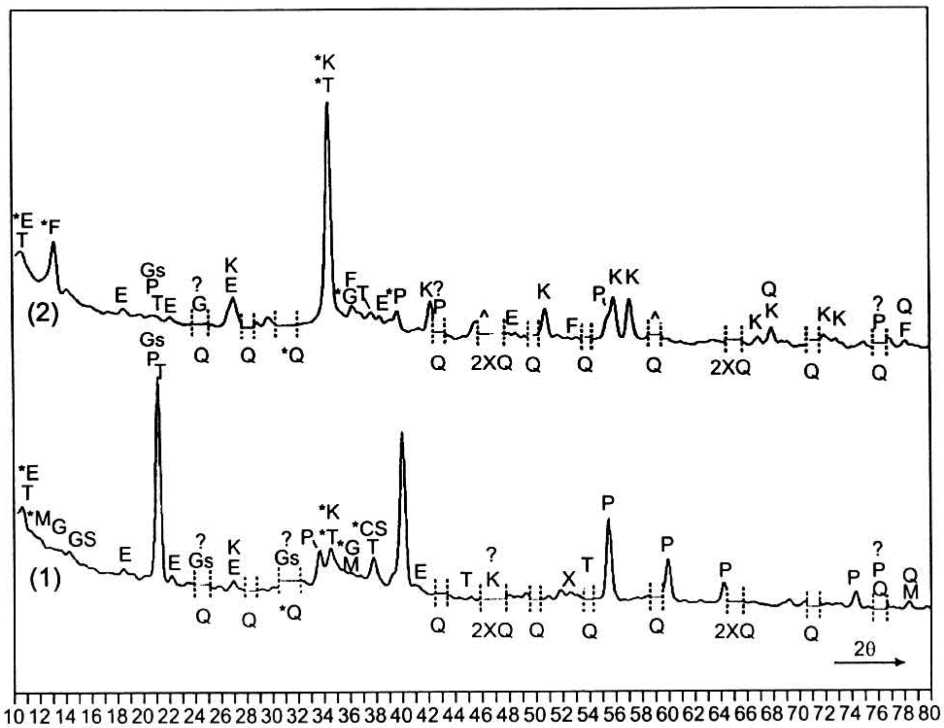

Fig.5 A sample dyfractogram of HSR cement phases from water environment and 4-mole chloride environment. 1 – water environment; 2 – aggressive chloride environment

The dyfractograms were carefully analyzed. A range of phase compositions listings were made and the changes within them were specified. This allowed to classify the resistance of OPC, MSR and HSR cements.

5. The research results analysis

5.1. The corrosion resistance rates values

On the basis of the data contained in Tables 2, 3 i 4 analysis it can be stated that for the sulfate and 1- and 4-mole chloride environments, in comparison to comparative water environment the decrease in strength, which is dependent on the time, can be observed.

For CEM I 42,5 NA HSR cement, after the initial (1 month) sealing of the structure, a slow decrease in the corrosion resistance and bending strength appears. In the Portland cement CEM I 42,5 the alternate sealing processes (the corrosion resistance rates CR increase) and cracking of the structure inside the samples (the corrosion resistance rates CR decrease) can be noticed.

After 24 months both cements still show a good resistance to the sulfates action. In the CEM I 42,5 NA HSR cement the corrosion processes course is much slower. No cracks or peeling can be observed on the surface of the samples made from both cements. After 36 months, however the CEM I 42,5 HSR NA cement reaches the corrosion resistance rate value (CR = 0,751), which varies by a small extent from the limiting value (CR = 0.75). For the ordinary Portland cement this value is much lower (CR = 0.643).

For aggressive chloride environment with the 1- and 4-mole concentration a short, initial period of sealing the structure a decrease of the CR rate. Sealing (an increase of the CR value) appears at various points of time for each of the cements. This proves, that differences in the chemical reactions between the hydrates of the cements and the components of aggressive environments. The phenomena of cement stone structures sealing and the destructive processes appear at different points of time and their range is also various.

This research also shows, that the CEM I 42,5 MSR NA and CEM I 42,5 HSR NA cements give much better final effects than usual cement. The HSR and MSR cements mechanical characteristics are about 20% higher values both in comparative water environment and in aggressive deicing salts environment than those for the ordinary Portland cement. The CR rates are, however, lower than in the case of sulfate ions influence.

5.2. Scanning microscopy

The following statements are based of the photos taken analysis.

In the samples produced from the examined cements, stored in comparative water environment the same phases (portlandite, ettryngite,tobermorite) were observed, but the crystal shape and the amounts were different.

The samples made from the usual CEM I 42 NA Portland cement contain the short-fibre ettryngite, relatively small amounts of gel tobermorite, portlandite and calcite.

The samples made from the CEM I 42.5 HSR NA cement contain gel tobermorite, the fine-crystalline ettryngite, relatively small amounts of portlandite, and calcite. The observed structure is more compact than of the samples made from CEM I 42 NA Portland cement.

The samples made from the CEM I 42.5 MSR NA cement contain ettryngite, tabular portlandite, gel and fine-crystalline tobermorite.

The samples form the aggressive environments distinctly show the products of the reactions between the examined cements and the environments components, which significantly differ depending on the kind of cement, and for:

- sulfate environment :
  - CEM I 42.5 NA – large amounts of short-, medium- and long-fibre ettryngite (thin and thick crystallites), small amounts of monosulfate, small amounts of gypsum are visible, the structure is loose.
  - CEM I 42.5 HSR NA – thin, short-, and medium-fibre ettryngite, large amounts of gel forms, the structure is more compact than in Portland and road cement,
  - CEM I 42.5 MSR NA – wispy, medium- and long-fibre ettryngite, gel forms are present, the damage to the structure is visible.
- 1-mole chloride environment :
  - CEM I 42.5 NA – Friedel's salt grains are visible, ettryngite, small amounts of alkaline calcium chloride, gel forms are present, the structure is visibly damaged, cracks are present.
  - CEM I 42.5 HSR NA – Friedel's salt grains are visible, fine ettryngite, tobermorite, infinitesimal amounts of alkaline calcium chloride, portlandite, the structure is less damaged, than in case of usual Portland cement,
  - CEM I 42.5 MSR NA – small Friedel's salt grains are visible, very fine ettryngite, infinitesimal amounts of alkaline calcium chloride, the structure is less damaged, than in cases of usual Portland cement or HSR cement,
- 4-mole chloride environment :
  - CEM I 42.5 NA – Friedel's salt grains are visible, small amounts of alkaline calcium chloride, ettryngite, the structure is visibly damaged, loose, numerous cracks are present.
  - CEM I 42.5 HSR NA – Friedel's salt grains are visible, alkaline calcium chloride, very fine ettryngite, gel forms are present, the structure is more compact than in cases of Portland and road cement,
  - less damaged, than in case of ordinary Portland cement, tobermorite, infinitesimal amounts of portlandite,
  - CEM I 42.5 MSR NA – Friedel's salt grains are visible, alkaline calcium chloride, very fine ettryngite, gel forms are present, the structure is damaged – cracks are present, the structure is more compact than in case of usual Portland cement .

5.3. X-ray structural rating

During the research larger portlandite binding in the samples made of CEM I 42.5 HSR NA and CEM I 42.5 MSR NA cements than in the ones produced from CEM I 42,5 NA Portland cement. In the aggressive sulphate environment the least of ettryngite and the most of C-S-H phases was observed in the samples made from CEM I 42.5 HSR NA cement and less in samples made from CEM I 42.5 MSR NA cement.

In all examined mortars from chloride environment significant wash-out of cement phases can be observed, as well as the presence of crystalline phases, characteristic for these environments, causing the destruction of the samples.

The largest amounts of ettryngite, Friedel's salts and alkaline calcium chloride are present in the samples made from CEM I 42,5 NA Portland cement.

In both aggressive chloride environments the CEM I 42.5 HSR NA cement contains larger amount of Friedel's salts than cement.

In aggressive chloride environment with 1-mole concentration in the samples made from CEM I 42.5 HSR NA cement a larger amount of alkaline calcium chloride was detected than in the samples made from CEM I 42.5 MSR NA cement.

In aggressive chloride environment with 4-mole concentration the samples made from CEM I 42.5 HSR NA cement the smallest amount of alkaline calcium chloride was detected.

6. Conclusions

The research of three class CEM I 42,5 NA cements, produced serially, stored in clean water environment and in aggressive sulfate and chloride environments showed the following dependences:

- the mortars made of usual Portland cement are the least durable in the environments listed above,
- in the sulfate environments the durability can be represented with the following dependence:
  $CR_{36\,m}$ for HSR > MSR > OP i.e.: 0.751 > 0.744 > 0.643,
- in the 4-mole chloride environments the durability can be represented with the following dependence: $CR_{36\,m}$ for HSR > MSR > OP i.e.: 0.561> 0.541 > 0.523.

The serially produced sulfate resistant HSR and MSR cements are much less resistant to deicing salts environments than in the sulfate environments anticipated for them. In that case it would be reasonable to agree with the thesis of [5], which states, that for the environments of deicing salts other groups of cements should be recommended, for example CEM II, not CEM I, even the special ones.

7. References

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