Study of the properties of chemically resistant repair mortar with the use of secondary raw materials

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Abstract. This paper deals with the research of a new silicate-based repair mortar modified with selected secondary raw materials. The aim of this work is to develop a chemically resistant material suitable for use in an extremely aggressive environment of sewers. The monitored parameters include key physical-mechanical characteristics, resistance to sulphate ions and to the attack of aggressive biogenic sulfuric acid. Chemical resistance was tested by simulating the exposure environment in laboratory conditions, according to the methodology of DIN 19573. The obtained results show that by suitable modification of the reference mortar it is possible to maintain the values of physical-mechanical characteristics and improve the chemical resistance of test samples.

1. Introduction

The sewerage system represents a characteristic exposure environment with high requirements for the durability of used building materials. When remediation sewers, the aim is to restore or extend the original service life of the entire building structure. Repair mortars intended primarily for the reprofiling of the damaged concrete surface represent a main material in the remediation of the useful properties of the remediated building structure. The requirements for this type of mortar are, among other things, easy applicability, high strength, resistance to mechanical damage and resistance to chemically aggressive environments.

The service life of a concrete structure is significantly shortened due to chemical degradation. The rapid degradation of cement composites in the environment of sewers is mainly due to the fact that due to their chemical composition and high calcium content they have limited resistance to acid attacks [1]. Conventional concrete sewer elements do not have significantly increased chemical resistance. New concrete elements should be treated with secondary protection in the form of a chemically resistant coating before installation into the structure. During remediation, the application of these coatings is complicated due to the increased humidity.

Problems with corrosion of concrete waste systems have been known since the beginning of the last century [2, 3]. In some cases, the service life of concrete drains is limited to less than 10 years [2]. The high concentration of H_2S (Hydrogen sulfide) in sewers has the greatest effect on reducing the service life of concrete structures. Hydrogen sulfide is formed by the decomposition of organic matter in sewage by anaerobic bacteria found in the sewer system. If there is a sufficient amount of oxygen in the fluid, chemical and biological processes take place that oxidize H_2S to e.g. H_2SO_4 [4].

The process of biocorrosion of concrete can be described in three steps: Neutralization of the concrete surface, which creates a suitable environment for the growth of appropriate bacteria oxidizing sulfur

compounds. This occurs in an environment with a higher concentration of H_2S. Fresh concrete can reach values in the range of pH 11-13, while acid gases reach pH <6. In the next step, the H_2S on the surface of the sewer oxidizes. This can occur not only biologically but also chemically. In both cases, it is an aerobic process in which two molecules of oxygen (O_2) are attached to oxygen-free hydrogen sulfide (H_2S) to form sulfuric acid (H_2SO_4). In the third step, a reaction occurs between H_2SO_4 and the hydration products of the cement [5]. The reaction of sulphates and sulphites on the concrete surface most often takes place by the reaction of portlandite ($CaOH_2$) and other minerals. These are very complex physical and chemical processes [6], they include microscopic processes (diffusion of sulfates and sulfites, formation of new products with lower strengths or expansion character in pores and capillaries and the associated development of crystallization pressure), and macroscopic processes (gradual disintegration of cement composite). [7, 8]. Characteristic minerals formed during this type of cement composite degradation include gypsum ($CaSO_4 \cdot 2H_2O$) and ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26(H_2O)$.

The formation of these minerals is accompanied by significant volume changes, as the newly formed compounds contain a large amount of mainly water molecules, which were not contained in the original compounds. For example, the formation of gypsum increases the volume to 124% of the original volume of the mineral and the formation of ettringite even to 227% of the original volume [9], other sources indicate the expansion of ettringite by up to 700% of the original volume [10].

The process of concrete degradation due to the attack of sulphates or sulphites is accelerated by cyclic drying and wetting of the composite [11] and the ambient temperature also has a very significant effect [12].

A many of researches are focused on the possibilities of reducing the degradation of cement composites due to sulphates and sulphites by partial substitution of Portland cement with suitable additives or secondary raw materials. [13, 14] It was found that pozzolanic additives (high temperature fly ash, silica fume, metakaolin, etc.) have a positive effect on the structure of cement composite, pore distribution or their size. However, the results of other studies show [15] that, despite this positive effect of the addition of secondary raw materials, a negative effect on sulphate corrosion resistance may increase with increasing binder substitution rate. The aim is therefore to find the optimal degree of substitution of the cement binder with suitable secondary raw materials.

Due to the expensive remediation work, materials and technologies with sufficient durability but they must also be affordable. Thus, cement-based materials are still a suitable alternative, making it one of the most widely used variants of remediation systems. However, suitable materials must be selected for the design of such remediation materials. There is currently no comprehensive standard in Europe that provides information on materials suitable for use in these exposure conditions. However, there are several national standards that address the design of exposure concentration levels to define exposure classes related to aggressive chemical environments. [4] An example is the German standard DIN 19573 [16], which includes the design of exposure environments for chemically aggressive solutions of Na_2SO_4 and H_2SO_4 with defined concentrations, as well as requirements for tested materials based on cement binder.

2. Experimental details

2.1. Materials

The results presented in this work focus on the design and study of selected characteristics of raw material variants of cement-based repair mortar for the remediation of concrete sewer structures. This development is part of the cooperation between Brno University of Technology, the Faculty of Civil Engineering and a renowned manufacturer of building materials. The mentioned project is still ongoing, that is why only approximate mixtures are shown in Table 1. For the same reason, Table 1 only summarizes the composition of the mixture of admixtures, which includes, for example, plasticizers, crystalline admixtures, polypropylene fibers, and other admixtures. The mixture of the repair mortar is designed to function in the intended remediation system as a high-quality remediation mortar for manual application on small areas or for the repair of more complex profiles.

The aim of the project is to modify the existing mortar to meet the requirements for repair mortars according to DIN 19753 [16]. The reference mass (RM-ref) is a commercially available Portland

cement-based repair mortar which does not have any increased chemical resistance. The reference mass was modified by partial substitution of the binder with selected secondary raw materials (high temperature fly ash (A), amphibolite filler (B) and Thermal power plant slag (C)) in the amount of 10 to 30%. Individual modified raw material variants whose results are presented in this work are marked RM-10(20, 30) -A(B, C). For example, mixture RM-20-A is a repair mortar with 20% binder substitution by fly ash. In other respects, the composition of the raw material variants is similar to that of the reference mass.

The fly ash used meets the requirements for fly ash for construction purposes in accordance with Czech standard ČSN 72 2071. Amphibolite filler (further: filler) is a secondary raw material from the treatment of aggregates in the quarry. This secondary raw material was used in the form supplied by the producer. Thermal power plant slag, or coal slag (further: slag) was delivered in a fraction of 0−8 mm. Pre−treatment of slag for research purposes began by adjusting it to a 0–4 mm fraction using a jaw crusher. In the next step, the slag was adjusted to predetermined specific surface area 450 m^2/kg (± 50 m^2/kg). This value of the specific surface area corresponds to the value measured for the substituted cement. The grinding drum for discontinuous grinding was selected for grinding.

Table 1. Approximate composition of test recipes of repair mortar mixtures.

Raw material	The average proportion of raw materials in the developed mixture (wt.%)	
Cement CEM I – 42.5 R	20.3	30.6
Mixture of admixtures (wt.% of m_c) [a]	0.84	1.84
Secondary raw material [b]	2.9	10.2
Finely ground limestone	3.0	6.0
Silica sand 0.18 – 1.0	34.0	37.0
Silica sand 0.6 – 1.0	17.0	21.0
Silica sand 1.0 – 4.0	3.0	6.0

[a] Mixture of plasticizers, crystalline admixtures, other admixtures and polypropylene fibers.
[b] Substitution of cement in the rate of 10-30%, depending on the type of secondary raw material: A - fly ash, B - amphibolite filler, C – coal slag.

2.2. Fabrication of test specimens

For the correct interaction of all components contained in the repair mortar, all input raw materials were homogenized using a container homogenizer. To ensure perfect mixing of all raw materials, the minimum homogenization time was set at 30 minutes.

The production of the fresh mixture was carried out in accordance with standard EN 196 -1: 2016. The mixing time was 270 ± 5 seconds. After mixing, the consistency of the fresh mortar was determined in according with standard EN 1015-3. The water / cement ratio (w) was chosen so that the consistency of the individual fresh mortars corresponds to the selected optimal consistency of 137.5 ± 5 mm. The influence of the additive of individual secondary raw materials on the consumption of mixing water was negligible and the value of "w" was almost identical for all tested mixtures.

All fabrication was performed in a laboratory mixer with forced circulation at the set speed in accordance with the standard ČSN EN 196-1 and in laboratory conditions (23 ± 2 °C, 55 ± 5% relative humidity). The setting of the mixer was chosen for perfect mixing of the dry mixture with the mixing water and activation of the powder admixtures by intensive mixing. All fabricated test specimens were cured for 24 h at more than 90% humidity and temperature of 20 ± 1 °C, before being demolded and after that were cured in water until the measurements were made.

2.3. Test methods

2.3.1. Physical-mechanical characteristics. As mentioned above, the consistency of fresh mortars was determined according to EN 1015-3. The compressive strength was measured in accordance with EN 12190:1998. Mortar specimens were fabricated with dimensions of 40 mm × 40 mm × 160 mm and the compressive strength of the repair mortars was tested at an age of 28 days. The water absorption of

the test specimens was subsequently determined on fractions of these test specimens. The water absorption was measured in accordance with Czech standard ČSN 72 2448.

2.3.2. Test for sulphate resistance. The test specimens (10 × 40 × 160 mm) were exposed to an aggressive sulphate solution with a concentration of 29.8 g / l (44 g / l Na_2SO_4) for 91 days. To measure the length changes, measuring pegs were attached to the surface of the test specimens. These measuring pegs and the entire measurement process were in accordance with EN 12617-4.

The reference specimens were left throughout the exposure only in a saturated solution of $Ca(OH)_2$. Initial length between measuring pegs were measured and recorded at an age of 60 ± 3 days. Length changes of test specimens were recorded at regular intervals, and standard DIN 19573 define boundary value for length change ($\Delta\varepsilon$ <0.8 mm / m), which is determined by comparing test specimens exposed to both environments.

2.3.3. Test for resistance to biogenic sulphuric acid attack. A solution of sulfuric acid (H_2SO_4) with a concentration of pH = 0 ($c(H_2SO_4)$ =1.0 mol / l) was used to determine of the chemical resistance of repair mortars to biogenic sulphuric acid attack. The test specimens (40 × 40 × 80 mm) were exposed to a chemically aggressive solution for 14 days.

The test for resistance to biogenic sulfuric acid attack was started at the age of the test specimens of 60 ± 3 days. The pH value of the bath is checked and kept constantly topped up by titration on a daily basis. At the end of storage in acid, any loose material is cleaned off the test samples with a soft brass wire brush under running water. Prisms of h = 40 mm (± 1 mm) are sawn from the middle of each of these prisms. The cut surfaces are ground square and parallel. Reference prisms are prepared from the reference specimens in the same way. After storage for 2 days at 21ºC (± 2º) and at 60% (± 10%) relative humidity, compressive strength is measured using the compression test as per EN 196 -1:2016.

The relative residual compressive strength of the corroded mortar test samples is used as the measure of the level of corrosion. Relative residual compressive strength is the residual compressive strength of corroded mortar specimens compared to the compressive strength of specimens after the equivalent length of time stored under water.

The effective depth of corrosion $X_{f,D}$, related to compressive strength, is obtained from the test load applied the corroded prisms at the end of testing and the test load on the reference prisms that have meanwhile been stored in water.

3. Evaluation of Experimental Testing

The results of the determination of the compressive strength and water absorption of 28-day-old test specimens are given in table 2.

Table 2. Selected physical–mechanical properties of individual developed mixtures.

Developed mixtures	Water absorption (%)	Compressive Strength (N/mm^2)
RM-ref	7.1	76
RM-10-A	7.8	76
RM-10-B	8.1	57
RM-10-C	7.5	71
RM-20-A	8.4	73
RM-20-B	8.6	52
RM-20-C	8.1	67
RM-30-A	9.1	61
RM-30-B	9.5	40
RM-30-C	8.8	58

The compressive strength of the test specimens of the modified mixtures decreased with increasing degree of cement substitution. However, even with the substitution of 30% of the cement with fly ash, the compressive strength decreased by only 20% after 28 days of maturation, and with the 30% coal slag

admixture, the compressive strength decreased by 24%. In the case of 20% cement substitution, there was only a negligible decrease in compressive strength in most raw material variants. The water absorption has also achieved good results in the case of mixtures with a medium degree of binder substitution. In view of the above, a 20% cement substitution rate was chosen as optimal for chemical resistance testing.

The course of deformation of the test specimens exposed to Na_2SO_4 solution for 91 days is represented graphically in figure 1.

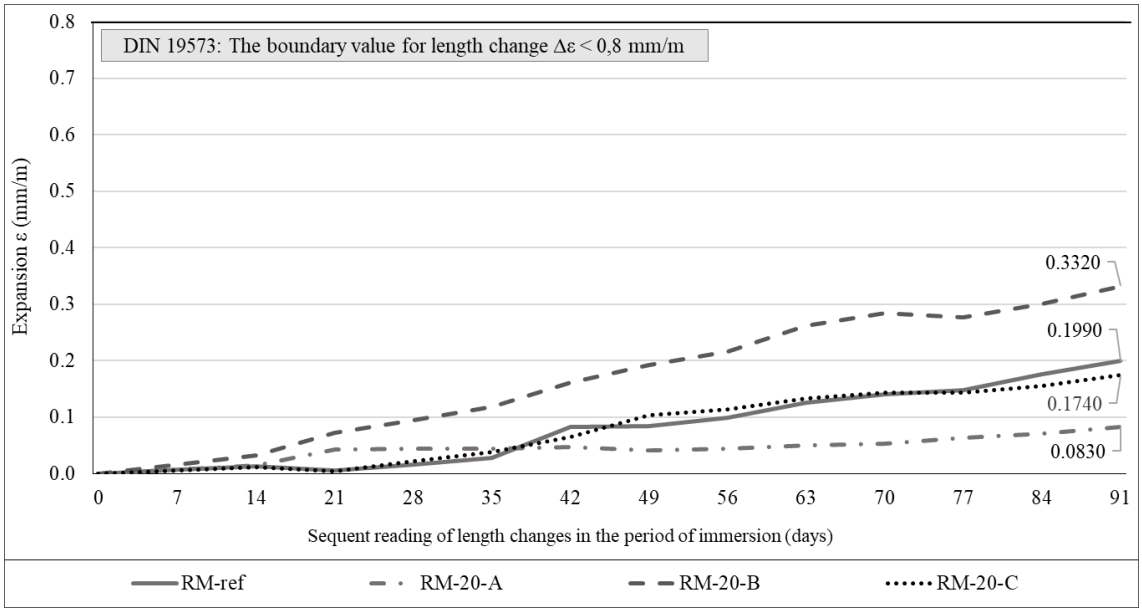

Figure 1. Graphical representation of the course of deformation of test specimens exposed to sulphates in time.

The results of the determination of the sulphate resistance of the test samples of the treated mixtures show that the resistance to external sulphate attack was the highest in the mixture with 20% substitution of cement by fly ash. Compared to the reference mixture, RM-20-A mortar showed a 58% reduction in the length change of the test specimens after 91 days of exposure. In the case of the RM-20-C mixture (mass with coal slag) there was a reduction in length changes of 12% compared to the reference mixture.

The next Figure 2 graphically presents the results of determining the relative residual compressive strength of corroded test specimens exposed to an aggressive solution of sulfuric acid at a concentration of pH = 0 ($c(H_2SO_4)$ =1.0mol / l) for 14 days. Standard DIN 19573 defines that the minimum relative residual strength of chemically resistant repair mortars must be > 55% for this exposure solution.

It is clear from the above results that the resistance of the modified mixtures to biogenic sulphuric acid attack does not compare with the previous results of resistance to attack by the sulphate solution.

When compared with the reference mortar, the highest relative residual compressive strength was determined for RM-20-B, which is a repair mortar with the addition of amphibolite filler (5% increase in strength). The lowest measured value was determined for the mixture with the addition of fly ash (8% decrease in strength).

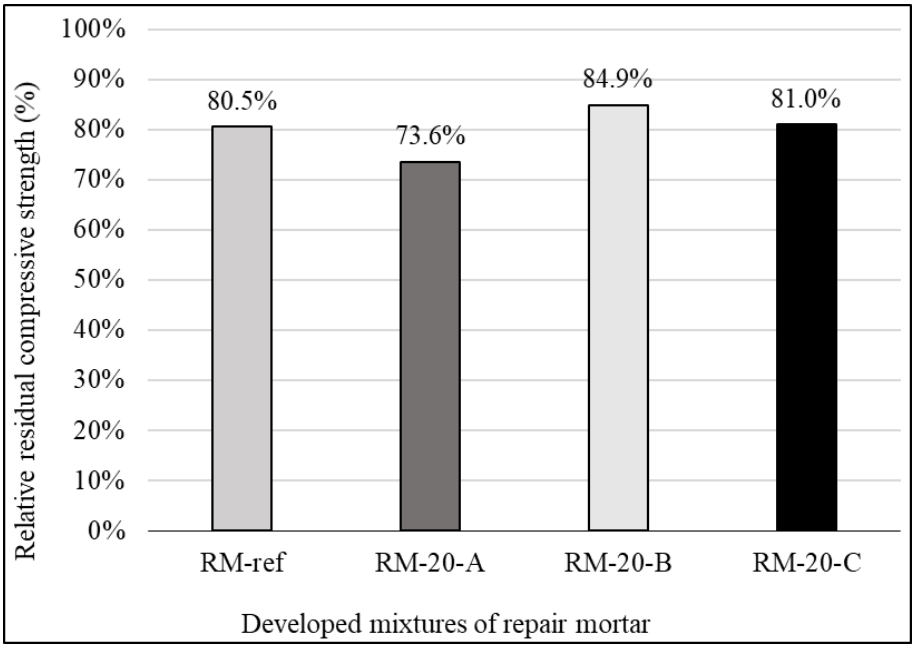

Figure 2. Graphical representation of the relative residual compressive strength of the corroded mortar test samples after exposed to a chemically aggressive solution of sulfuric acid (H_2SO_4) with a concentration of pH = 0 (c(H_2SO_4) =1.0mol / l) for 14 days.

4. Conclusion

The aim of this work was to verify the properties of new mixtures for chemically resistant repair mortar modified by the additive of selected secondary raw materials. Based on DIN 19573, several specific apparatuses for testing the chemical resistance of test specimens have been assembled. These devices have been optimized for research purposes.

Based on previous research, a set of repair mortar mixtures modified by partial substitution of the cement binder with potentially suitable secondary raw materials was compiled. The properties of the individual mixtures were assessed on the basis of experimental tests. The result of this work is an optimal mixture for a new chemically resistant repair mortar.

The results of this work show that it is possible to successfully increase the chemical resistance of the developed repair mortar by partial substitution of the cement binder with suitable secondary raw materials. The effect of individual secondary raw materials differed depending on the observed physical-mechanical characteristics or type of chemically aggressive environment.

From the results it can be deduced that the most balanced results were achieved in the case of the mixture RM-20-C. This is a mixture with 20% substitution of cement by coal slag. This mortar was characterized by low water absorption, great compressive strength and also it achieved an improvement in chemical resistance compared to the reference mortar, in both tested exposure environments.

The next phase of research and development of the new mortar will focus on a detailed study of the influence of individual secondary raw materials on the properties of the repair mortar with emphasis on the resistance to sulphate attack and biogenic sulfuric acid attack. Among other things, the influence of secondary raw materials on the structure of the cement composite and the formation of corrosion products will be evaluated.

The existing set of laboratory analyses will be extended by a complex of physicochemical analyses for a more detailed characterisation of the evolving corrosion processes.

5. References

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