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ANALYSIS OF SULFATE RESISTANCE OF CONCRETE WITH RCA AFTER ONE YEAR EXPOSURE TO SULFATE SOLUTIONS*

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Abstract. *External sulfate attack is one of the durability problems associated with concrete. Despite a perception that concrete made with recycle concrete aggregate (RCA) is of inferior quality, research has shown that RCA has the potential to satisfy the mechanical and physical requirements for a range of applications. Limited works were performed on the durability aspects of the RCA. The objective of the research described in this paper was to evaluate resistance to sulfate attack of concrete with RCA in which two types of cement (CEM I and CEM III) and two water to cement ratios (0.38 and 0.55) were combined. For the evaluation of sulfate resistance of these concretes, immersed in sodium and potassium sulfate solutions, a drop of compressive strength, length change, capillary water absorption and thermal analysis (TGA-DTA) were used. Satisfactory sulfate resistance of concrete with RCA can be achieved by applying CEM III and reducing water to cement ratios.*

Key words: *sulfate attack, recycled concrete aggregate (RCA), TGA-DTA, length change, capillary water absorption*.

1. INTRODUCTION

The construction industry contains many activities that yield a high carbon footprint i.e., manufacturing of Portland cement (OPC) and crushed aggregates, transportation of materials to the site, etc. [1]. Also, the growing demand for construction materials during the urbanization process has already affected the nature aggregate and other non-renewable resources increasingly depleted in many regions around the world. The construction of large-scale infrastructures, industrial plants, and residential buildings accompanied by the demolition of old buildings led to fast accumulation of construction and demolition wastes (C&DW), which has posed increasing threats to local environments, human health, as well as the already depleted landfills in cities. Recycled aggregate concrete (RAC) which uses recycled aggregate produced from C&DW as a partial or complete substitution to the virgin

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aggregate provides a solution to both the rising demand for construction materials and the excessive discharge of C&DW [2].

Research on RAC has been carried out for many years, and it has been widely recognized that the performance of RAC prepared with recycled coarse aggregate (RCA) is obviously inferior to that of the natural aggregate concrete (NAC) at the same mixture proportions. The presence of microcracks and residual cement paste results in the high porosity, low density and high-water absorption of RCA. However, a number of modification techniques were proposed for improving the RAC performance [2].

Degradation of concrete due to sulfate attack has been recognized as a serious issue for structures since long ago. Despite extensive research in this field, there is still many doubts and space for further research. Sulfate attack is a deteriorating process where sulfates ions react with the components of cement paste resulting in concrete deterioration over time. Sulfate attack in concrete can manifest in the form of spalling, expansion, cracking, increased permeability, and strength loss. The degree of resistance against the external sulfates depends on many factors such as chemical composition of components, mineralogy, reactivity, porosity of matrix etc.

In general, it can be stated that there is a lack of papers on the durability of concrete with RCA, especially in an aggressive environment. Some of researches have begun to investigate the degradation and performance of concrete with RCA under sulfate attack. Kazmi et al. demonstrated that the resistance of concrete with RCA to sulfate attack is lower than that with natural aggregate. Qing et al. reported that the addition of RCA reduces the deterioration of concrete under sulfate attack when the RCA replacement is at a low level; however, the results are opposite if the replacement rate of RCA is increased [3].

The paper presents the results of the resistance to sulfate attack of concrete that combined different cement types (CEM I and CEM III, according to EN 197-1), water to cement ratio (0.38 and 0.55) and type of coarse aggregate (natural river (NA) and recycled concrete (RCA)). For the evaluation of sulfate resistance of these concretes, the following testing methods were used on laboratory specimens immersed in sulfate solutions (5% Na2SO4 or 5% MgSO4) for 365 days: compressive strength, length change, capillary water absorption and thermogravimetric analysis (TGA-DTA, for samples with RCA).

2. EXPERIMENTAL INVESTIGATION

2.1. Component materials and mixture proportion

In order to investigate the effects of type cement, type aggregate and water to cement ration on sulfate resistance of concrete, four concrete mixtures were prepared with following component materials:

- Cement: Portland cement CEM I 42.5R (Lafarge-BFC Serbia, γ_{sc}=3100 kg/m^3) and Low heat/sulfate resistance cement CEM III/B 32.5N LH/SR (Lafarge-BFC Serbia, γ_{sc}=2650 kg/m^3),
- Aggregate: fine aggregate (river aggregate, 0/4 mm) and coarse aggregate (river aggregate, 4/8 and 8/16mm and recycled concrete aggregate, 4/8 and 8/16mm),
- Chemical admixture: HRWRA ("Sika ViscoCrete 3070", "Sika"- Switzerland),
- Tap water.

The basic physical properties of cement were tested according to standards EN 196-1 [4], EN 196-3 [5] and EN 196-6 [6].

Also, the basic characteristics of aggregate were examined. Recommendations and benchmark values for aggregate quality are given in standards EN 206 [7] and EN 12620 [8]. The origin of concrete mix design in RCA was unknown.

Designed compositions of concrete mixtures are shown in Table 1.

Table 1 Labels and mixture proportion of concrete in kg/m^3

Concretes (mixtures)	m_c CEM I	m_c CEM III	m_v	$m_{v,ad}$	$m_{a,f}$	$m_{a,c}$	m_{spk}	w/c
NPC1	350	-	195.5	-	930	858	-	0.55
NPC2	423	-	161	-	936	864	5.9	0.38
NMC1	-	338	186	-	936	864	0.7	0.55
NMC2	-	416	158	-	937	865	2.5	0.38
RPC1	350	-	192.5	20.2	874	803	-	0.55
RPC2	425	-	162	20.2	880	813	3.4	0.38
RMC1	-	338	186	20.5	881	813	-	0.55
RMC2	-	414	157	20.5	881	814	3.3	0.38

m_c-quantity of cement; m_v-quantity of water; $m_{v,ad}$-additional quantity of water that was calculated on the basis of RCA water absorption (2.5%); $m_{a,f}$-quantity of fine aggregate; $m_{a,c}$-quantity of coarse aggregate; m_{spk}-quantity of super-plasticizer; w/c-water-cement ratio

2.2. Curing, specimen preparation and labels

For all selected testing the following types of concrete specimens were prepared from each mixture:

- 150 mm cubes for compressive strength at age of 28 days (designated as 0)
- 100 mm diameter x100 mm height cylinders for compressive strength at 180 and 365 days after immersing the specimens into the sulfate solutions
- 100 mm x100 mm x 500 mm prisms for measuring length change
- 150 mm x150 mm x75 mm slabs for testing capillary water absorption.

All specimens were cured in lime-saturated water for 28 days. After that period, compressive strength was determined by testing three specimens from each mixture (150 mm cubes). One third of the remained specimens were transferred to containers with 5% Na_2SO_4 and another third in 5% $MgSO_4$ solution where they were stored until testing periods (90, 180 and 365 days). The last third of specimens were submerged in lime-saturated solution for the same periods (reference specimens).

For each mixture and for each solution, three specimens were tested.

Labelling was done in three series with four letters and one number in the following way: those with the first letter "E" were cured in lime-saturated water solution all the time, those with "N" were immersed in 5% Na_2SO_4 solution and those with "M" were stored in 5% $MgSO_4$ solution. The second letter in the label indicates the type of aggregate: "N" is natural aggregate and "R" is recycled concrete aggregate. The third letter refers to the type of cement: "PC" stands for CEM I and "MC" stands for CEM III. And the last letter denotes w/c ratio:"1" is for w/c=0.55 and "2" is for w/c=0.38. The value of compressive strength at the age of 28 days was taken as the initial value labelled as 0, meaning that the time of exposure to different conditions (sulfate and lime-saturated solutions) started from this point.

2.3. Methods

Compressive strength was tested according to EN 12390-3 [9] before the specimens were immersed in sulfate solutions and after storing them in these solutions for 90, 180 and 365 days.

The length change was measured continuously according to the procedure given in UNI 11307.

Testing of capillary water absorption were performed on specimens before were immersed in sulfate solutions and at chosen time.

TGA-DTA tests (Setaram, Labsys Evo) with a balance accuracy of 0.1μg, were performed on the specimens of ~30mg, crushed material, by heating in alumina crucible, 20-1000°C, at 10°C/min heating rate under argon atmosphere.

3. Results and Discussion

3.1. Compressive strength

The average results of concrete compressive strength after 90, 180 and 365 days of immersion in Na_2SO_4, $MgSO_4$, and lime-saturated water are presented in Table 2. In this table are also presented the strength values prior to the exposure to sulfate solutions at 28 days (in table 0 days).

Table 2 Compressive strength (MPa) of specimens

Concrete series	0 days	90 days	180 days	365 days	Concrete series	0 days	90 days	180 days	365 days
ENPC1	46.3	54.4	55.1	56.3	ENMC1	31.8	45.3	46.4	47.7
NNPC1		55.8	42.9	27.6	NNMC1		43.4	46.1	47.8
MNPC1		56.3	52.3	48.8	MNMC1		43.3	42.5	44.3
ENPC2	72.5	79.3	87.9	90.7	ENMC2	52.8	70.0	71.4	71.7
NNPC2		80.7	79.7	84.3	NNMC2		62.6	64.7	69.2
MNPC2		81.1	71.5	76.8	MNMC2		76.0	74.7	73.4
ERPC1	43.1	53.5	54.5	57.1	ERMC1	31.3	39.7	45.9	48.8
NRPC1		49.1	35.9	22.7	NRMC1		43.2	46.7	48.8
MRPC1		54.8	49.3	40.6	MRMC1		41.6	42.5	43.5
ERPC2	61.8	78.0	82.2	84.6	ERMC2	54.1	71.2	74.4	76.9
NRPC2		79.3	74.8	76.0	NRMC2		65.7	67.7	68.1
MRPC2		77.1	73.4	74.1	MRMC2		67.8	67.5	67.9

From the results in the Table 2 it can be concluded that almost all concretes have an increase in compressive strength after all observed periods of exposure to Na_2SO_4 or $MgSO_4$ solutions (90, 180 and 365 days) corresponding to reference specimens (28 days). The exception are concretes with CEM I and w/c=0.55 immersed in Na_2SO_4 and $MgSO_4$ solutions for 180 and 365 days.

For the better understanding, relative compressive strength values are illustrated in Figure 1. These values present the relation between the compressive strength of specimens immersed in selected sulfate solution and their corresponding reference values of the same age.

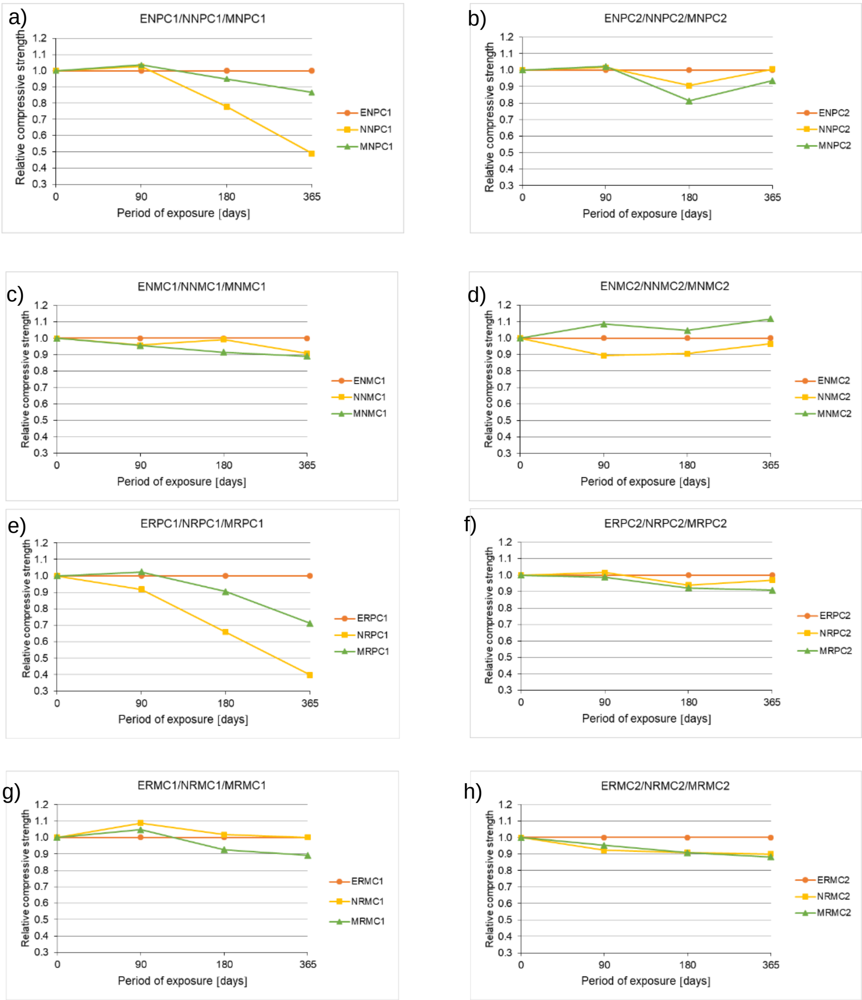

Fig. 1 Changes of compressive strength of concretes exposed to sulfate solutions in relation to corresponding strength of control specimens (a – NA, CEM I, w/c=0.55, b – NA, CEM I, w/c=0.38, c – NA, CEM III, w/c=0.55, d – NA, CEM III, w/c=0.38, e – RCA, CEM I, w/c=0.55, f – RCA, CEM I, w/c=0.38, g – RCA, CEM III, w/c=0.55, h – RCA, CEM III, w/c=0.38)

After 180 days of immersion in Na_2SO_4 or $MgSO_4$ solutions, all concretes with cement CEM I regardless of the type of aggregate and w/c ratio showed a decrease in strength compared to reference series (ENPC1, ENPC2, ERPC1, ERPC2), Figure 1. The concretes with w/c=0.55 which were immersed in 5% Na_2SO_4 solution (series NNPC1 and NRPC1) have the greatest decrease of compressive strength (22% for NNPC1, Figure 1a, and 34% for NRPC1, Figure 1e).

Concretes with CEM I regardless of the type of aggregate and w/c ratio, after 365 days of immersion in Na_2SO_4 or $MgSO_4$ solutions had a decrease in compressive strength compared to reference series. Two concretes with w/c=0.55 regardless the type of aggregate, which were immersed in 5% Na_2SO_4 solution (series NNPC1 and NRPC1) and one concrete with the same w/c and RCA immersed in 5% $MgSO_4$ (series MRPC1) had the greatest decrease of compressive strength. These decreases are 51% for NNPC1, 60% for NRPC1 and 29% for MRPC1.

The specimens of all concretes made with CEM III and stored in both sulfate solutions, showed differences in compressive strength at the age of 90, 180 and 365 days compared to reference series. Similar conclusion can be derived after 90, 180 and 365 days of exposure to both sulfate solutions: most concrete series showed a change in compressive strength, which did not exceed 10%, compared to the corresponding referent value. It can be seen that, after 365 days, the decrease in compressive strength of concrete series with RCA is slightly higher (MRMC1, NRMC2 and MRMC2) in comparison to the concrete with NA (MNMC1, NNMC2 and MNMC2).

3.2. Length change

Figure 2 shows the results of experiments monitoring the length changes of the concrete prisms subjected to 5% Na_2SO_4 and 5% $MgSO_4$ solutions, as well as the control specimens, which grouped according to the type of sulfate solution.

It can be seen that the linear expansion of concretes with CEM I, w/c=0.55 and both types of aggregate (series NNPC1, MNPC1, NRPC1, MRPC1), which have the largest values of linear expansion, depends on the type of sulfate solution. The difference between linear expansions of concretes made with RCA and NA is significant in the case of immersion in Na_2SO_4 (series NNPC1 and NRPC1). On the other hand, analysed difference is negligible when $MgSO_4$ is used (series MNPC1and MRPC1).

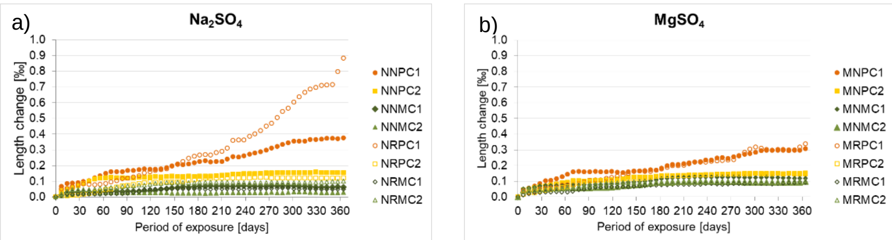

Fig. 2 Length change of concrete mixtures depends on sulfate solution a) in 5% Na_2SO_4; b) in 5% $MgSO_4$

3.3. Capillary water absorption

Results of capillary water absorption at 25 hours in kg/m^2 on all observed specimens after 180 and 365 days immersed in sulfate solutions are presented in Figure 3.

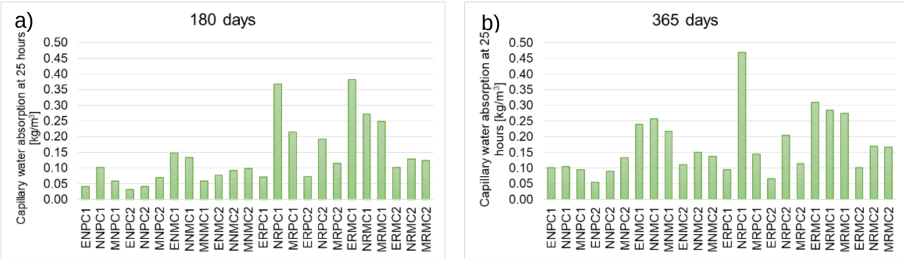

Fig. 3 Capillary water absorption of concrete mixtures depends on time exposure at 25 hours a) 180 days; b) 365 days

Due to different and complex physical processes and chemical reactions that occur during immersion specimens in sodium sulfate and magnesium sulfate solutions, analysis obtained results of capillary water absorption is not easy.

Nevertheless, on the basis of shown results some general conclusions can be drawn:

- The values of capillary water absorption are significantly affected by the type of aggregate, type of cement and the water to cement ratio.
- In general, mixtures with natural aggregate have lower values of capillary water absorption.
- The largest values of capillary water absorption, for specimens that have been exposed to sulfate solutions for 180 and 365 days, have the specimens with RCA and w/c=0.55 immersed in Na_2SO_4.

From the Figure 3, it can be seen that in all concrete specimens that were exposed to the sulfate solution, there was an increase in capillary water absorption over time, except for the samples with RCA, CEM I and w/c=0.55 immersed in $MgSO_4$.

3.4. Thermal analysis

Figure 4 presents TGA-DTA curves for samples with RCA that were exposed to sulfate solutions for 365 days. The thermal decomposition behaviour shows several characteristic temperature ranges that can be identified according to the DTA peaks and TGA curves. The mass changes and emphasized endothermic peaks up to 250 °C are generally assumed to be evaporation processes of physically and chemically bound water. Samples exposed to the sulfate solutions have significant peak about 150°C that are believed to be due to gypsum. The most intense peak at this point has the sample MRPC1 and also the highest loss in this temperature range (20°C-300°C). One new peak noticed at about 100°C for NRPC2 and MRPC2 and it may probably be assigned to ettringite.

Other significant peaks are between 400°C and 500°C primarily due to dehydration of portlandite. It can be seen that this peak is not present in samples with a higher water to cement factor (0.55, samples with number 1), while it is observed in samples with a lower water to cement factor (0.35, samples with number 2). Also, it is observed that samples MRPC1 and MRPC2 have one additional peak about 400°C that may be assigned to brucite (it is characteristically formed on the surface of samples exposed to the action of magnesium sulfate).

The weight loss in the range 500-900°C is probably related to the decomposition of some type of carbonates, that are inevitable. Thus, the weight loss associated with broad peak at ≈600°C is likely due to the decomposition of amorphous carbonated phases while peak at ≈780°C is probably due to decomposition some type of crystalized calcite.

The total mass loss (from 20°C to 1000°C) for observed specimens is the highest for NRPC1 (19.6%) and MRPC1 (20.6%) but the lowest for MRMC2 (12.7%).

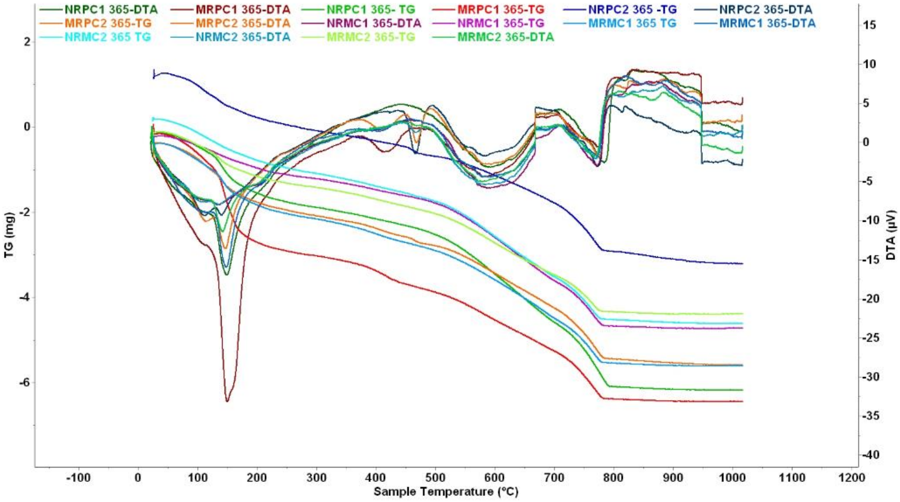

Fig. 4 TGA-DTA of samples with RCA exposed to solutions for 365 days

4. CONCLUSION

From the research that has been carried out in this study, it can be concluded that:

- The concretes made with CEM I and with w/c=0.55 which were immersed in both sulfate solutions have the greatest decrease of compressive strength, this is especially pronounced in samples exposed to the action of sodium sulfate. Other examined concretes showed changes in compressive strength up to 10% regardless of cement type, w/c ratio and sulfate solution type.
- In the case of a length change, the situation is very similar to the change in compressive strength. The concretes made with CEM I and with w/c=0.55, immersed in both sulfate solutions, have the greatest linear expansion. All other concretes have linear expansion significantly below.
- Due to different and complex physical processes and chemical reactions that occur during immersion specimens in sulfate solutions, it is not easy to draw a conclusion about the sulfate resistance of concrete based on the results of capillary water absorption. Generally, mixtures with natural aggregate have lower values of capillary water absorption.
- The results of the thermal analysis can be related to the results of the change in length. The samples with the greatest length change also had the greatest mass loss determined by TGA. As well, those samples also have the most pronounced peaks that are probably associated with the products responsible for the expansion of samples exposed to the action of sulfate solutions.

Generally, the type of cement, water to cement ratio and type of aggregate have effect on concrete sulfate resistance. The greatest influence on concrete sulfate resistance has cement type and type of aggregate. Water to cement ratio has minor influence on sulfate resistance in concrete with cement CEM III. However, in concrete with cement CEM I w/c ratio has significant influence on sulfate resistance. Satisfactory sulfate resistance of concrete with RCA can be achieved by applying CEM III and reducing w/c.

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ANALIZA OTPORNOSTI BETONA SA RCA NA DEJSTVO SULFATA NAKON JEDNOGODIŠNJE IZLOŽENOSTI SULFATNIM RASTVORIMA

Spoljašnje dejstvo napad sulfata je jedan od problema vezanih za izdržljivost betona. Uprkos percepciji da je beton napravljen od recikliranog agregata za beton (RCA) lošijeg kvaliteta, istraživanja su pokazala da RCA ima potencijal da zadovolji mehaničke i fizičke zahteve za niz primena. Ograničeni radovi su obavljeni na aspektima trajnosti RCA. Cilj istraživanja opisanog u ovom radu bio je da se proceni otpornost betona sa RCA na dejstvo sulfata u kome su kombinovane dve vrste cementa (CEM I i CEM III) i dva vodocementna faktora (0,38 i 0,55). Za procenu sulfatne otpornosti ovih betona, potopljenih u rastvore natrijum i kalijum sulfata, korišćen je pad pritisne čvrstoće, promena dužine, kapilarna vodoapsorpcija i termička analiza (TGA-DTA). Zadovoljavajuća otpornost betona sa RCA na sulfate može se postići primenom CEM III i smanjenjem vodocementnog faktora

Ključne reči: *sulfatno desjstvo, reciklirani betonski agregat (RCA), TGA-DTA, promena dužine, kapilarno upijanje vode.*