Evaluation of sulfate resistance of concrete with recycled and natural aggregates

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HIGHLIGHTS

- Sulfate resistance of concretes made of RCA (5% Na_2SO_4 and 5% $MgSO_4$ solutions).
- RCA could be used for preparation of sulfate resistant concrete.
- Concrete microstructure changes analized by SEM, BSE-EDS, XRD and FTIR analyses.

ARTICLE INFO

ABSTRACT

The paper deals with the results of sulfate resistance of eight concrete mixtures with coarse recycled concrete aggregate/natural aggregate, CEMI/CEMIII and two different water-to-cement ratios (w/c). These concretes were immersed in 5% Na_2SO_4 or 5% $MgSO_4$ solutions for 90, 180 and 365 days. The evaluation of sulfate resistance was done by determination of compressive strength and length change. Concrete specimens submerged in both solutions up to 365 days, containing recycled concrete aggregate, CEM III and both w/c ratios, showed good resistance to sulfate attack. Characteristics related to microstructure (SEM, BSE-EDS, XRD and FTIR) were analysed on the concrete which was not sulfate resistant.

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1. Introduction

The construction industry, as one of the largest industries in the world, entails a significant consumption of both energy and raw materials and, consequently, the emission of CO_2 into the atmosphere. This negative impact on the environment should be minimised as much as possible. To ensure this, it is necessary to apply lifecycle and sustainable engineering approaches to concrete mix design [1]. This requires several elements: maximizing concrete durability, conservation of materials, the use of waste and supplementary cementing materials, and recycling of materials [2]. This approach has been included into the European Union policy intended at promoting the use of recycled aggregates in concrete production up to 70% until 2020 (EU directive) [3].

The use of aggregate obtained from crushed concrete is an example of recycling and conservation of raw materials [2]. This

may be one of significant efforts in achieving a sustainable construction. The major difference between natural aggregate and recycled concrete aggregate (RCA) is the presence of adhered mortar on the surface of the original natural aggregate [4]. Adhered mortar is regarded as porous material containing sand, hydration products and unhydrated cement grains. Its porous structure is open and aggressive external ions can be more easily transported into RCA concrete, imposing the risk of chemical attack [5]. Most of the studies have been focused on the mechanical or microstructural characteristics of concrete containing recycled aggregate (RA), while very few publications can be found in the literature that discuss durability aspects of the concrete with RCA [2,6–8]. Recycled concrete aggregates are generally regarded to be weaker than corresponding virgin aggregate in terms of mechanical, physical and chemical action [9]. Due to this weakness, the use of RCA is very limited especially in the case when the concrete structure is required to have high strength and/or high durability [10]. Despite the perception that the concrete made with RCA is inherently of inferior quality, research has shown that RCA has the potential to

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satisfy mechanical and physical requirements for a range of applications [2,7,11,12]. In addition, it is well established that concrete shows good sulfate resistance when it is made of sulfate-resistant cement and has good quality due to compactness, and low permeability. Both the former promising research results regarding RCA durability and the latter mentioned practice data give the direction how to make sulfate resistant concrete with RCA.

The deterioration of concrete by external sulfate attack is commonly noticed in structures exposed to soils, groundwater, rivers, seawater and industrial wastes containing high concentration of sulfate ions [13]. This phenomenon leads to the transport of ions into the interior through pore structure and to the reaction with solid hydration products [14]. The conversion of the hydration products of cement to the harmful products such as ettringite, gypsum and thaumasite additionally leads to decalcification of calcium silicate hydrate (C-S-H) that causes weakening of the paste [15,16]. This influences softening, expansion and cracking of concrete [14]. The expansion resulting from sulfate attack is generally attributed to the formation of gypsum and ettringite, although there is some controversy surrounding the exact mechanisms causing the expansion [14,17,18]. This attack is very complex and it may be gradual, but it can cause serious damage to concrete structures [19]. Many factors can affect sulfate resistance such as cement composition [18,20–24], permeability of concrete, w/c ratio [21,25,26], cation type in sulfate salts [27], sulfate ions concentration [26], exposure conditions [24,27–29] and exposure period [23,30].

The most commonly occurring salts for sulfate resistance tests are sodium sulfate (Na_2SO_4) and magnesium sulfate ($MgSO_4$). These cation types (Na^+ or Mg^{2+}) related to sulfate ions define the mechanism of attack and significantly influence concrete deterioration [13]. Sodium sulfate (i.e. sulfate ion) reacts with hydration products of cements, resulting in the formation of ettringite ($3CaO·Al_2O_3·3CaSO_4·32\ H_2O$) and gypsum ($CaSO_4·2H_2O$) [31]. The provision of Ca^{2+} ions, necessary for ettringite and gypsum formation, is supplied by portlandite or by decalcification of C-S-H gel. Decalcification of C-S-H gel affects the loss of bonding. Gypsum is usually formed under mortar/concrete surface. In this region, aluminium ions are primarily consumed for the formation of ettringite and, therefore, sulfate ions can react only with the remained calcium ions [16] and form gypsum. The creation of gypsum is related to the spots where pH value is high. The interaction of ion species from $MgSO_4$ solution and hydration products of cements gives M-S-H gel and brucite ($Mg(OH)_2$) in addition to gypsum and ettringite, which are common reaction products in both solutions (Na_2SO_4, $MgSO_4$). M-S-H gel does not have binding capacity. In the presence of brucite, decalcification of C-S-H gel is more prominent due to brucite low solubility [32]. The saturated solution of brucite has a pH of 10.5, which is too low to maintain the stability of C-S-H, and the stability of calcium aluminate sulfate [13]. The reaction of $MgSO_4$ with calcium hydroxide is also followed by the formation of brucite layer on the specimen surface and gypsum under it. To mitigate this attack, concrete codes recommend a concrete mixture with low w/c ratio [21,33], containing sulfate-resistant Portland cement or Supplementary Cement Materials-SCM (fly ash, silica fume, slag) [12,21,33]. Slag is recognized as an efficient SCM in improving the sulfate resistance, particularly at a higher level of cement replacement, as in the case of CEM III. Slag hydrated products are similar to Portland cement one [34]. The most abundant is C-S-H with modified morphology [35] and lower C/S ratio than in PC [36]. Due to this C/S ratio, the degree to which aluminium replaces silicon is high. Additionally, hydrotalcite-like phase is formed, which is also the case with stratlingite in certain instances [37,38]. If the replacement level of Portland cement with slag in slag-blended cements increases, the amount of AFm, Aft (diluting effect) and CH decreases

[39,40]. A lowered availability of these compounds can reduce the damage caused by sulfate attack due to a direct reduction in the quantity of ettringite and gypsum [12,18,41]. Their formation extent is limited due to the lack of Ca^{2+} ion and due to the lack of aluminium ions forming monosulfate, the only one that can form ettringite. Namely, a part of aluminium ions are included into hydrotalcite or C-S-H gel structures, so the rest is enough to form only a small amount of monosulfate or ettringite. Also, slag can refine the pore size distribution and reduce the pore connectivity in mortar/concrete, which also contributes to the overall durability of concrete [42].

Most sulfate resistance testing has been undertaken on mortar or cement paste specimens [12,18,20,22,27,28,43,44] as concrete introduces additional variables and makes testing more difficult. Except for the type of materials (paste, mortar, concrete), the evaluation of sulfate resistance depends on: water to cement ratio, specimen dimensions and shape (prisms, cubes, cylinders), curing conditions before the exposure to sulfate solutions (immersion in water or lime-saturated water, duration of curing, humidity and temperature conditions), type and concentration of aggressive solutions and procedure of exposure to sulfate attack.

There are some recommendations for increasing the sulfate resistance of mortar/concrete [45–47] but currently there is no European standard which defines the experimental procedure for testing or criteria for sulfate resistance which should be met.

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 exposed to sulfate solutions (5% Na_2SO_4 and 5% $MgSO_4$): length changes, compressive strength, loss of mass, capillary water absorption, and microstructural analyses. This paper presents a part of these results, i.e. the results of compressive strength, length change of eight concrete mixtures which were immersed in sulfate solutions for 90, 180 and 365 days, the results of phase compositions (X-ray powder diffraction-XRD, Fourier Transform Infrared Spectroscopy-FTIR) and microstructure analyses (Scanning Electron Microscope-SEM and Backscattered Electron Imaging (BSE)-Energy Dispersive X-ray (EDS)) obtained only on specific specimens.

2. Experimental investigation

2.1. Materials and mixture proportion

To assess the influence of different aforementioned parameters on sulfate resistance of concrete, the following component materials were used:

- 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 8/16 mm and recycled concrete aggregate, 4/8 and 8/16 mm).
- Admixture: HRWRA ("SikaViscoCrete 3070", γ_s = 1090 kg/m^3 and "SikaViscoCrete 5500HP", γ_s = 1090 kg/m^3 "Sika" - Switzerland).
- Tap water.

The basic physical properties of cements were tested according to standards EN 196-1 [48], EN 196-3 [49] and EN 196-6 [50].