Abstract

This study investigates relationships between concrete containing pozzolanic additive and mineralogical composition, porosity and chemical durability to sulphate ion containing solution. As pozzolanic admixtures micro and nano size silica and biomass ashes were used. The investigation was carried out by X-ray diffraction, Hg absorption porosimetry and optical microscopy.

The pozzolanic additives activate the process of mineralization and are acting both as the cementitious admixture as well as the fine filler. The crystalline phases in all depths of the specimen, mass change, porosity were investigated after the exposure of concrete in sulphate ions containing solution for 1-6 months under static conditions. The way of sulphate attack depends on a pozzolanic additives and kind of sulphate solution. X-ray phase analysis of concrete in different depth after exposure in solution identified gypsum for concrete with additives only up to 10 mm.

The addition of fine dispersed additives decreases the number of pores in all range, especially in 1…10\(^3\) μm. Cementitious properties of pozzolanic materials and crystallization of sulphate salt in pores decrease number of pores in range 0.5…10\(^{-3}\) μm.

Studies have shown that the pozzolanic additives reduce porosity, increase density and as a consequence increase the chemical durability of concrete to sulphate ion containing solution.

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1. Introduction

Most of produced concrete today is conventional concrete with not very good indicators for corrosion resistance. Concrete corrosion is collapse of concrete matrix due to influence of physically – chemical processes of environment [1-2]. The deterioration of concrete structural components exposed to soils and groundwater contaminated with sulphate salts is a serious problem in durability of concrete. The sulphate ions react with the hydration products of cement, namely C\(_3\)A and Ca(OH)\(_2\), producing expansive and softening types of deterioration [3].

Interaction between SO\(_2\) and concrete can be proposed as process of many steps: SO\(_2\) diffusion through the sulfated surface to the depth of concrete—SO\(_2\) reaction with liquid phase forming H\(_2\)SO\(_4\) → oxidation to H\(_2\)SO\(_4\) → reaction of H\(_2\)SO\(_4\) with Ca(OH)\(_2\) forming gypsum CaSO\(_4\)·2H\(_2\)O. By gypsum formation the volume of solid phase increases 2 times what results in stress and cracks arising. The neutralization process of fine pore structure concrete can take place already on the initial stage; the densification and increase of the compressive strength is observed. In accordance with humidity (condensed water, air precipitate, technological liquid) accelerate spalling and decay of sulfated layers [4-5]. To prevent decay of concrete under action of aggressive agents various methods are suggested; as modifying concrete by addition of plastizers

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and mineral admixtures so well using coatings [6-8]. One way to improve chemical durability and mechanical properties of concrete is to add in composition fine dispersed cementitious materials.

One in them is pozzolana - a natural or artificial material containing silica or alumina (mainly silica) in a reactive form [9-10]. By themselves, pozzolanas have little or no cementitious properties. However, in a finely divided form and in the presence of moisture they will chemically react with alalis to form cementing compounds [11]. The silica and alumina in a pozzolana has to be amorphous, or glassy, to be reactive.

When silica containing e.g. fly ash is added to concrete the pozzolanic reaction occurs between the silica glass (SiO$_2$) and the calcium hydroxide Ca(OH)$_2$ or lime, which is a by-product of the hydration of Portland cement minerals and water. The hydration products produced fill the interstitial pores reducing the permeability of the matrix [12-13]. Due to limited solubility of hydration products, particles of hydrated lime form within interstitial spaces. With a continuing supply of moisture, the lime reacts with the fly ash pozzolancially, producing additional hydration products of a fine pore structure. The pozzolanic reaction is as in calcium hydroxide + silica = tricalcium silicate + water [14-15]:

$$3\text{Ca(OH)}_2 + \text{SiO}_2 = 3\text{CaO} \cdot \text{SiO}_2 + 3\text{H}_2\text{O}$$ (1)

This work deals with the investigation to reveal the influence of various pozzolanic admixtures on chemical durability of concrete.

2. Materials and methodology

For studies of the influence of pozzolanic admixtures to chemical resistance, several groups of concrete mix compositions were prepared, see Table 1.

Table 1. Composition of concrete specimens with different pozzolanic materials

| Component                      | Microsilica ELKEM, 30-450 nm | Micro/nano silica ELKEM, 30-450/15-100 nm | Wood ashes, <200μm | Wood+ barley straw ashes, <200μm |
|--------------------------------|-------------------------------|-------------------------------------------|--------------------|----------------------------------|
| 1.CEMI 52.5R [kg]              | 950                           | 950                                       | 700                | 700                              |
| 2.Sand0.3/2.5 mm [kg]          | 470                           | 470                                       | 370                | 370                              |
| 3.Sand 0/0.5 mm [kg]           | 200                           | 200                                       | 520                | 520                              |
| 4.Quartz powder, [kg]          | 340                           | 340                                       | 300                | 300                              |
| 5.Pozzolanic material. [kg]    | 150                           | 140/10                                    | 210                | 210                              |
| W/C ratio                      | 0.20                          | 0.20                                      | 0.26               | 0.26                             |

In order to achieve the better particle packing, mix of compositions were prepared, taking into account the grain size distribution of raw materials, i.e. the grading curves.

The specimens measuring 50×50×50 mm were prepared by mixing previously weighed amounts of raw materials; activated-type laboratory mixer was used. After demoulding, samples were cured in water for 28 days at +20 °C temperature. After that samples were exposed to laboratory conditions (+20 °C) for 2 month prior to tests.

Water and sulphate solutions absorption of specimens was tested according to LVS EN ISO 15148:2003.

Absorption of water and solutions containing SO$_4$$^2-$ (0.25 mol·l$^{-1}$) was tested: cubes were immersed in solution so that the solution level was 10 mm above the surface of specimens. The water uptake was measured by successive mass weightings, at regular intervals of 5 minutes in the first half hour of test, and later at every 10 minutes up to 2 hours, at every 30 minutes up to 5 hours of measurements.

The samples were immersed in water or solutions containing SO$_4$$^2-$ for period of 1-6 months under static conditions.

Chemical analysis of pozzolanic materials, concrete in different depth and sulphate solutions were determined according to LVS EN 196-2:2005.

pH of solutions after definite period of immersion of samples by Laboratory Jonometers WTW pH340 was measured.

Pozzolanic activity was determined by adapted chemical method by Costa and Massazza [16]. Amount of CaO were calculated.

Mineralogical composition of concrete specimens in different depth before and after immersion in solution was analysed by X-Ray Diffraction (diffractometer Rigaku Optima Plus) using Cu$_{Kα}$ radiation.

Surface area of pozzolanic materials was made by BET (‘‘Nova 1200 E-Series, Quantachrome Instruments’’), pore size distribution of concrete by Hg absorption porosimeter (Quantachrome Poremaster with effective range from 0,001 μm to 1000 μm).
Compressive strength of samples was determined by hydraulic press Controls Automax5. Load was applied with constant rate of 0.75 kN/s.

Morphology of samples was observed using microscope Leica M420.

3. Experimental

Natural and artificial pozzolanic additives were chosen in order to evaluate their influence to the properties of concrete: micro and nano size silica, ashes of biomass (wood ashes, wood + barley straw ashes).

Chemical composition of additives indicating high content of silica: for micro and nano size silica 98…99 mas.%, for biomass 50…60 mas. %. By XRD analysis of biomass ashes crystalline silica was detected: quartz and cristobalite as well as corresponding compounds of calcium silicate – wollastonite and akermanite. However micro and nano silica appeared to be X-ray amorphous.

Theoretically it could be suspected, that the presence of larger amount of amorphous phase leads to higher degree of pozzolanic reactivity. This correlates well with the data obtained by pozzolanic activity tests, when micro and nano silica demonstrated the higher values of pozzolanic activity [17].

Taylor [18] explains the hydration processes involved in some detail. The calcium hydroxide etches the surface of the glassy particles reacting with the SiO₂ or the Al₂O₃–SiO₂ framework. The hydration products formed reflect the composition of the pozzolanic additive, as well the values of Ca/Si ratio.

Independently from added pozzolana – either wood ashes, micro or nano silica after 90 days of hardening in concrete samples by X-ray diffraction haturite and tobermorite – calcium hydrogen silicate was identified, Fig. 1. Portlandite (Ca(OH)₂) for reference specimens only was identified.

Fig. 1. X-ray diffraction concrete with microsilica

Thus it could be concluded, that the pozzolanic additives activate the process of mineralization, what correlates well with the data obtained by pozzolanic activity test.

The measurements of physical properties by water and sulphate solutions (Na₂SO₄, H₂SO₄) absorption is rather simple method providing a lot of data. For the specimens containing pozzolanic additives, water absorption by capillarity and by total immersion was measured. The relationship between the absorbed water amount and the type and dispersity of applied pozzolanic additive was established. Additives are acting both as the cementitious admixture as well as the fine filler, filling up the pores, which are responsible for the migration of moisture.

Table 2. Properties of pozzolanic additives

| Nr | Pozzolanic material          | Calculated amount of CaO after 24h | Specific area, m²/g |
|----|------------------------------|-------------------------------------|---------------------|
| 1. | Wood ashes                   | $5.0 \times 10^{-2}$                | 2.869               |
| 2. | Wood ashes + barley straw    | $0.504 \times 10^{-2}$              | 3.787               |
| 3. | Microsilica                  | $6.944 \times 10^{-2}$              | 7.917               |
| 4. | Nanosilica                   | $9.184 \times 10^{-2}$              | 22.025              |
Pozzolanic activity, expressed as the amount of reactive CaO, was tested after 3 and after 24 hours of reaction with Ca(OH)$_2$, see Table 2.

Cumulative water and sulphate solution uptake decreases for concrete specimens with all kind of pozzolanic additives. Saturation does not exceed 0.6 mas. % at the same time saturation for reference specimens achieves ranges from 0.8 to 1 %. Nanosilica with most specific area presents lower saturation. Cumulative water uptake after 120 min. showed a linear relationship with the square root of time in minutes.

The next step of investigation was simulation of sulphate solution attack on concrete and evaluation of corrosion process depending on pozzolanic admixture and pH solution.

After 6 months of exposure in neutral solution of Na$_2$SO$_4$ (pH 6.5) on the surface all concrete specimens showed no signs of corrosion, Fig. 2b.

Different results were obtained after exposure in sulfuric acid solution (pH 1.5). Due to corrosion process of concrete heterogeneous surface with a white precipitate has formed, Fig. 2a. X-ray phase analysis shows crystalline compound - gypsum, formed according to the equation:

\[
\text{Ca(OH)}_2 + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 2\text{OH}^- \tag{2}
\]

The penetration of water and SO$_4^{2-}$ containing solution is in straight proportion to admixture (pozzolana) of specimens and time of exposure.

Using fine dispersion cementitious materials allow to obtain concretes with pores of smaller dimensions and, consequently of larger durability, this subject started to deserve increasing prominence.
Pores with dimensions larger than 0.1 μm contribute to the mass transport by diffusion, ionic migration, capillarity and permeability, while the smaller pores only influence the process of gaseous diffusion and sorption and of ionic diffusion and migration.

Concrete specimens after exposure in sulphate solutions were examined by microscopy and by X-ray phase analysis in different depth to establish formation of sulfate compounds on the surface of concrete and salt diffusion depth into concrete.

![Fig. 4. Scheme of investigation: 1 – surface; 2 – in depth 12.5 mm; 3 – in depth 25 mm](image)

Intensity diffusion of sulfate solution depends on the nature of the additive. Fine additives with the cementitious properties fill the large pores and prevent the penetration of sulfate ion in the sample. Figure 5a shows the formation of gypsum in to fine pores of the samples without fine additives. Figures 5 b, c show that the addition of pozzolanic materials (wood ashes or micro/nanosilica) form a dense structure, which limits the sulfate ion transport and subsequent reaction with Ca(OH)$_2$ and gypsum formation.

![Fig. 5. Microphotography of concrete (a), concrete with wood ashes (b); micro/nanosilica (c) after sulphate solution attack simulation in H$_2$SO$_4$ for 200 day in 10 mm depth. Magnification 40×.](image)

The formation of gypsum can lead to further deleterious reactions in the cement matrix. Gypsum may react also with other cement phases forming 3CaO.Al$_2$O$_3$.3CaSO$_4$.32H$_2$O (ettringite) or Ca$_6$[Si(OH)$_6$]$_2$.CO$_3$.3(SO$_4$)$_2$.22H$_2$O (thaumasite).

X-ray phase analysis in different depth of concrete has shown that the mineralogical composition of concrete does not change after exposure in 0.25 M Na$_2$SO$_4$, H$_2$SO$_4$ solutions. Before and after the exposure in SO$_4^{2-}$ containing solutions the following crystalline phases of concrete have been defined: quartz, calcium silicate. Regardless of pozzolana dosage after the exposure gypsum was found both at the surface of the specimen and in depth to 10 mm, which is most probably due to corrosion. Increasing dispersion of chemical composition stopped penetration of sulphate ions in concrete at 5-6 mm, Fig. 6.
Regardless of the composition of concrete there was observed similar causal relationship:

- exposing the concrete samples in neutral solution (H₂O, Na₂SO₄), mainly carbonation and hydration processes took place, which results in weight gain of specimens by adding all kind of pozzolana. After passing water hydration resulted in weight gain up to 2.10%, but after the passing of sulphate ions containing solutions is mainly determined by increase in mass up to 1.70 % due to crystallization of salts on the surface and into pores.
- after exposure in acidic solution containing sulphate ions occur interaction according to the reaction (2). The aggressive action of sulfuric acid increases washing Ca(OH)₂ out of concrete specimens, resulting in the loss of weight of pozzolana containing specimens: for microsilica - 2.10%; for wood ashes – 2.45%; for wood + barley straw ashes – 2.64%; for reference specimens - > 4.50%. After exposure for 200 hours pH solutions increase from 1.5 up to 7.

Pore size distribution was analyzed with pozzolanic additives before and after samples exposure to sulphate ion solution. Reference concrete samples characterized heterogeneous structure with pore in large size from 10⁻³ up to 10³ μm, Fig. 7. The addition of fine dispersed additives decreases the number of pores in all range. Especially decreases number of large pores in range of 1…10¹ μm. Fine pozzolanic additives operates as filler as well as cementitious material, see Fig.8.
Pore distribution of concrete specimens after exposure to sulphate solution has changed. Mainly pore volume and size increased for reference concrete specimens. This is due to aggressive action of sulphates to concrete, as a result of destruction of the concrete structure.

The total porosity of pozzolanic additives containing concrete, regardless of the solution (Na$_2$SO$_4$ or H$_2$SO$_4$) in all cases decreases. It is related to the ongoing processes of hydration and crystallization of salt in pores, Fig. 9. It can be seen that the concrete maturation process continues – it is an active system. Cementitious properties of pozzolanic materials and crystallization sulphate salt in pores decrease number of pores in range 0.5…10$^{-3}$ μm. Surface area of specimens has exposed corrosion process in depth up to 10 mm.

Compressive strength of samples after exposure in sulphate solution remains at invariable value – 85…95 MPa. The results showed that the addition of pozzolanic materials obtained high-strength concrete - a material with high chemical resistance which can be recommended for use in structures requiring high chemical resistance.

**Conclusions**

Pozzolanic activity of the concrete admixtures strongly depends on their chemical composition, amount of reactive silica as well as the specific surface area.

The pozzolanic additives (mikro/nanosilica, wood ashes) activate the process of mineralization of concrete minerals – tobermorite, haftrurite were identified.

Finely dispersed pozzolanic additives play a role micro fillers and supplementary cementitious materials and result as decrease of number of pores.

The solution of sulphuric acid causes significant damage of concrete. Reference concrete samples have heterogeneous structure with pore in large size from 10$^{-3}$ up to 10$^{3}$ μm. Fine dispersed additives decrease the number of large pores in range 1…10$^{3}$ μm.

After exposure of concrete with pozzolanic additives in SO$_4^{2-}$ containing solutions general crystalline phases remain and those are: quartz, calcium silicates. Gypsum on surface and in depth up to 10 mm of specimens is identified.
The results obtained in this study have shown that micro/nanosilica and wood ashes are the potential additives for enhancing the properties of concrete. Due to their chemical composition, they contribute to reactions of pozzolana and development of the concrete durability.

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