



Investigating the chemical durability of concrete produced with pozzolanic additives

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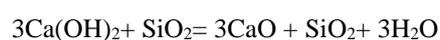
Abstract: *This study investigates the behavior of concrete produced with pozzolanic additives in the presence of sulphate ion containing solution. Pozzolanic admixtures of micro and nano size silica and biomass ashes were used in this study. The investigation was carried out by X-ray diffraction, Hg absorption porosimetry and optical microscopy. The crystalline phases at all depths of the specimen, mass change, and porosity were investigated after the exposure of concrete in sulphate ions containing solution for a period of 1-6 months under static conditions. Results revealed that the pozzolanic additives seem to activate the process of mineralization and acting both as cementitious admixture as well as fine filler. X-ray phase analysis of specimens at different depths after exposure in solution showed the formation of gypsum in specimen with additives only up to 10 mm. The addition of fine dispersed additives decreases the number of pores in all range, but more strongly in the 1-10³µm range. Cementitious properties of pozzolanic materials and crystallization of sulphate salt in pores decrease the number of pores in the range 0.5-10⁻³µm. This study has therefore shown that the pozzolanic additives reduce porosity, increase density and as a consequence increase the chemical durability of concrete in the presence of sulphate ion containing solution.*

Keywords: concrete; pozzolana; additives; chemical composition; durability; chemical corrosion; porosity; crystalline phase.

1.0 Introduction

Studies have shown that most conventional concretes produced today lack good corrosion resistance. Concrete corrosion is the collapse of concrete matrix due to its interaction with the physicochemical processes within the environment [1-2]. The deterioration of concrete as structural components when exposed to soils and groundwater which are contaminated with sulphate salts poses serious problem in terms of its durability. The sulphate ions react with the hydration products of cement, namely C₃A and Ca(OH)₂, thereby resulting in expansive and softening types of deterioration [3].

The interaction between SO₂ and concrete is a process involving many steps: SO₂ diffuses through the sulfated surface to the depth of concrete → SO₂ reacts with liquid phase forming H₂SO₃ → oxidation to H₂SO₄ → reaction of H₂SO₄ with Ca(OH)₂ forming gypsum CaSO₄·2H₂O. The formation of gypsum causes the volume of the solid phase to double thereby imposing stress which leads to cracks [4-5]. To prevent decay of concrete under the action of aggressive agents various methods are suggested [6-8]. One way is by modifying the concrete by addition of plastizers and mineral admixtures. Chemical durability and mechanical properties of concrete can also be improved by adding in the composition fine dispersed cementitious materials. One of such is pozzolana; a natural or artificial material containing silica or alumina (mainly silica) in a reactive form [9-10]. By themselves, pozzolans have little or no cementitious properties. However, in a finely divided form and in the presence of moisture they will chemically react with alkalis to form cementing compounds [11]. The silica and alumina in a pozzolana has to be amorphous or glassy, to be reactive. When silica containing substance such as fly ash is added to concrete, the pozzolanic reaction occurs between the silica glass (SiO₂) 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 are formed within interstitial spaces. With a continuing supply of moisture, the lime reacts with the fly ash pozzolanicly, producing additional hydration products of a fine pore structure through the following chemical reaction [14-15]:



(1)

This work seeks to investigate the influence of various pozzolanic admixtures on chemical durability of concrete.

2.0 Materials and methodology

To study the effect of pozzolanic admixtures on chemical resistance, several group of concrete mix compositions were prepared as shown in Table 1.

Table 1: Composition of concrete specimens with different pozzolanic materials

Component	Micro-silica 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
1. Sand 0/0.5 mm [kg]	200	200	520	520
2. Quartz powder, [kg]	340	340	300	300
3. Pozzolanic material. [kg]	150	140/10	210	210
W/C ratio	0.20	0.20	0.26	0.26

In order to achieve good 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 using activated-type laboratory mixer. After demoulding, samples were cured in water for 28 days at +20°C temperature. The 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 with cubes which 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 weighing, at regular intervals of 5 minutes in the first half hour of test, and later at every 10 minutes up to 2 hours, and then 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 at different depths and sulphate solutions were determined according to LVS EN 196-2:2005. The pH of solutions after definite period of immersion of samples was measured by means of the Laboratory Jonmeters WTW pH340. Pozzolanic activity was determined by adapted chemical method employed by Costa and Massazza [16]. The amounts of CaO were also calculated.

Mineralogical composition of concrete specimens at different depth before and after immersion in solution was analyzed by X-Ray Diffraction (diffractometer Rigaku Optima Plus) using $\text{Cu}_K\alpha$ 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 at constant rate of 0.75 kN/s. Morphology of samples was observed using microscope Leica M420.

3. Results and Discussion

Natural and artificial pozzolanic additives such as micro and nano size silica, ashes of biomass (wood ashes, wood + barley straw ashes) were chosen in order to evaluate their influence on the properties of concrete. The chemical analysis of additives indicates high silica content; for micro and nano size silica, it was found to be 98-99 mas.%, for biomass, it was 50-60 mas.%. Furthermore, the XRD analysis of biomass ashes revealed the presence of crystalline silica such as quartz and cristobalite as well as corresponding compounds of calcium silicate like wollastonite and akermanite. However micro and nano silica appeared to be X-ray amorphous.

Theoretically, it is expected that the presence of large amount of amorphous phase silica leads to high degree of pozzolanic reactivity. This correlates well with the result obtained from the pozzolanic activity tests where micro and nano silica addition showed high values of pozzolanic activity [17].

According to Taylor [18] during the hydration processes, calcium hydroxide etches the surface of the glassy particles reacting with the SiO_2 or the Al_2O_3 - SiO_2 framework. The hydration products formed reflect the composition of the pozzolanic additive, as well the values of Ca/Si ratio. Results of X-ray diffraction of concretes produced with all the pozzolanic additives under investigation after 90 days of hardening revealed thathatrurite and tobermorite – calcium hydrogen silicate were found as shown in Fig. 1. For the reference specimens however, only Portlandite ($\text{Ca}(\text{OH})_2$) was found.

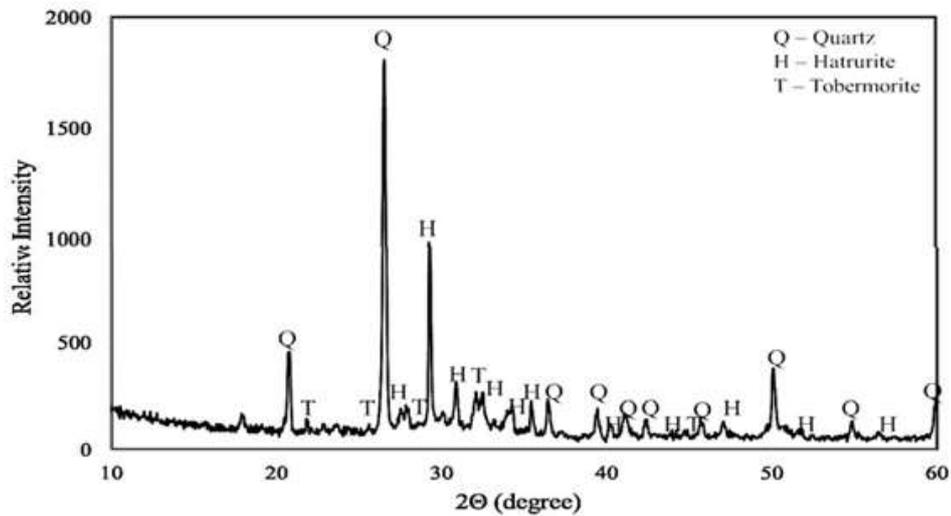


Fig. 1: X-ray diffraction of concrete with micro-silica

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

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 disparity of applied pozzolanic additive was established (see Table 2). Additives were acting both as the cementitious admixture as well as the fine filler, filling up the pores, which is responsible for the migration of moisture.

Table 2: Result of pozzolanic activity test for pozzolanic Materials Utilized

N r	Pozzolanic material	Calculated amount of CaO after 24 h	Specific area, m ² /g
1	Wood ash	5.0 X 10 ⁻²	2.869
2	Wood ash + barley straw	0.504X 10 ⁻²	3.787
3	Micro-silica	6.944X 10 ⁻²	7.917
4	Nano-silica	9.184X 10 ⁻²	22.025

Pozzolanic activity, expressed as the amount of reactive CaO, was tested 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. It was discovered that saturation level did not exceed 0.6mas.% for the concrete with additives during the time the reference specimens had achieved saturation range of 0.8 to 1 mas.%. Nano-silica 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.

Fig. 2b shows the result obtained after 6 months of exposure in neutral solution of Na₂SO₄ (pH 6.5). It was observed that the surface of all the concrete specimens showed no sign of corrosion.



(a)

(b)

Fig. 2: Concrete with micro-silica after sulphate solution attack simulation in H₂SO₄ (a); Na₂SO₄ (b) for 200 days

A different result was observed after exposure in sulfuric acid solution (pH 1.5) as presented in fig. 2a. Due to corrosive action on concrete, a heterogeneous surface with a white precipitate has formed. Fig.3 presents the XRD patterns of surface of Concrete specimens containing micro-silica, wood ashes, and wood + barley straw ashes after exposure in sulphuric acid. The Microphotography of concrete specimens after sulphate solution exposure in H₂SO₄ for 200 day in 10 mm depth is shown in

fig.5a,b,c. X-ray phase analysis shows the formation of gypsum; a crystalline compound formed according to the following equation:

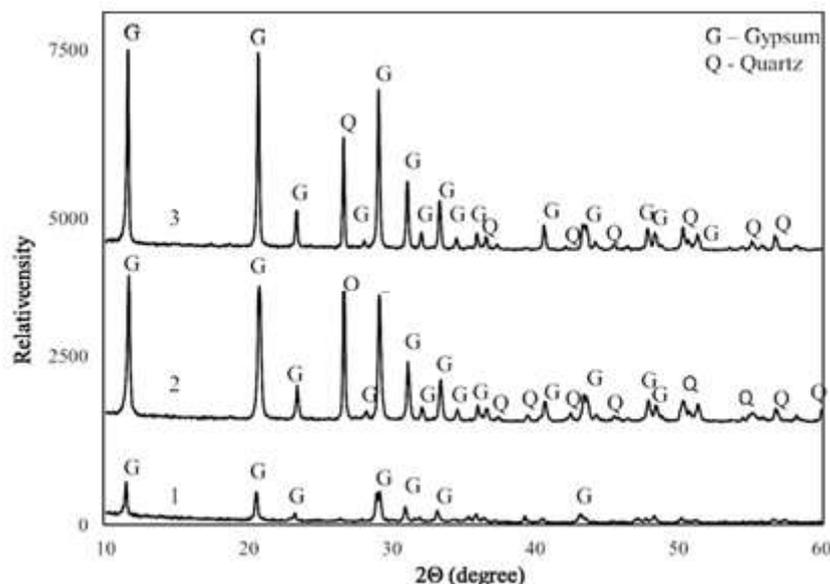
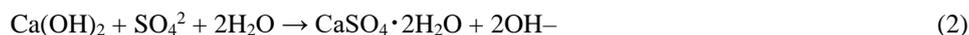


Fig. 3. XRD patterns of concrete surface after exposure in sulphuric acid. Concrete specimens containing: micro-silica (1); wood ashes (2); wood + barley straw ashes (3)

Results revealed that the penetration of water and SO_4^{2-} -containing solution is in direct proportion to the admixture (pozzolana) of specimens and time of exposure. Using fine dispersion cementitious materials allow the production of concretes with pores of smaller dimensions and, consequently, of longer durability.

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.

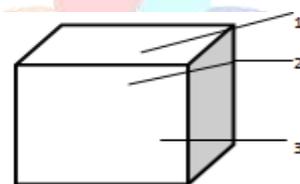


Fig. 4. Scheme of investigation: 1 – surface; 2 – in depth 12.5 mm; 3 – in depth 25 mm

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 fine pores of the samples without fine additives. Figures 5b, 5c show that the addition of pozzolanic materials (wood ashes or micro/nano-silica) form a dense structure, which limits the sulfate ion transport and subsequent reaction with Ca(OH)_2 and gypsum formation.

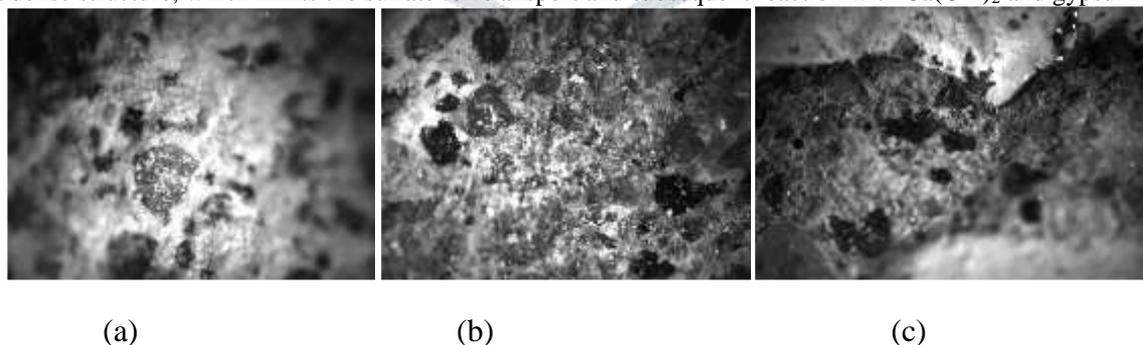


Fig. 5. Microphotography of concrete (a), concrete with wood ashes (b); micro/nanosilica (c) after sulphate solution attack simulation in H_2SO_4 for 200 day in 10 mm depth. Magnification 40×

The formation of gypsum can lead to further delirious reactions in the cement matrix. Gypsum may react also with other cement phases forming $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ (ettringite) or $\text{Ca}_6[\text{Si(OH)}_6]_2 \cdot \text{CO}_3 \cdot (\text{SO}_4)_2 \cdot 22\text{H}_2\text{O}$ (thaumasite). X-ray phase analysis for different depth of concrete has shown that the mineralogical composition of concrete does not change after exposure in 0.25M of Na_2SO_4 and H_2SO_4 solutions. Regardless of pozzolana dosage after the exposure, gypsum was found both at the surface of the specimen and in depth up 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 as seen in Fig.6.

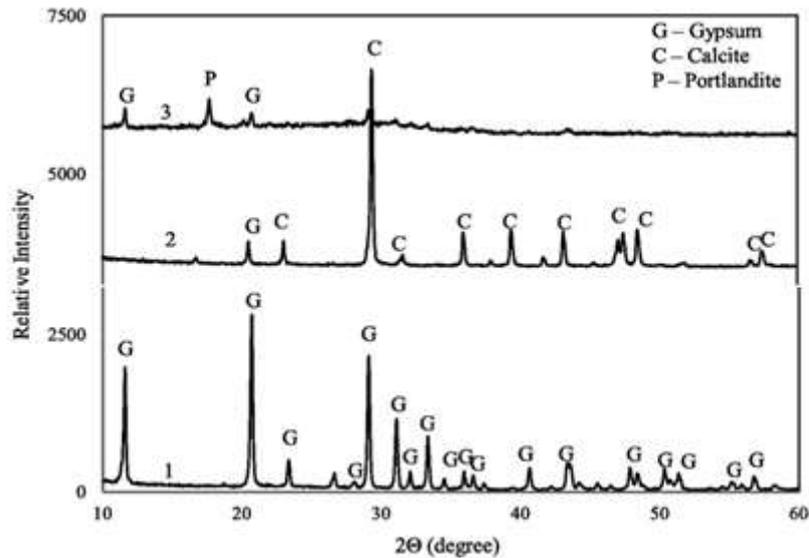


Fig. 6. XRD patterns of concrete at a depth of 10 mm after exposure in sulphuric acid. Additives: 1 – without; 2 – micro/nanosilica; 3 – wood ashes.

Regardless of the composition of concrete similar causal relationship were observed:

- ❖ Exposing the concrete samples in neutral solution (H_2O , Na_2SO_4), 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 of up to 2.10%, but after the passing of sulphate ions containing solutions, increase in mass of up to 1.70% due to crystallization of salts on the surface and into pores was observed.
- ❖ After exposure in acidic solution containing sulphate ions, the aggressive action of sulfuric acid intensifies the washing of $Ca(OH)_2$ out of concrete specimens, resulting in the loss of weight of pozzolana containing specimens. It was observed that for micro-silica, it was 2.10%; for wood ashes, 2.45%; for wood + barley straw ashes, 2.64%; for reference specimens, >4.50%. After exposure for 200 hours, the 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 and the result is as shown in fig.7. The Reference concrete samples were characterized with heterogeneous structure of pore sizes ranging from 10^{-3} up to $10^3 \mu m$.

Presented in fig.8 is the result of the pore size distribution analyses in concrete with different pozzolanic additives. The addition of fine dispersed additives revealed a decrease in the number of pores in all pore size ranges. Substantial decrease in the number of large pores in range of $1-10^3 \mu m$ was observed. This result suggest that fine pozzolanic additives operate as filler as well as cementitious material.

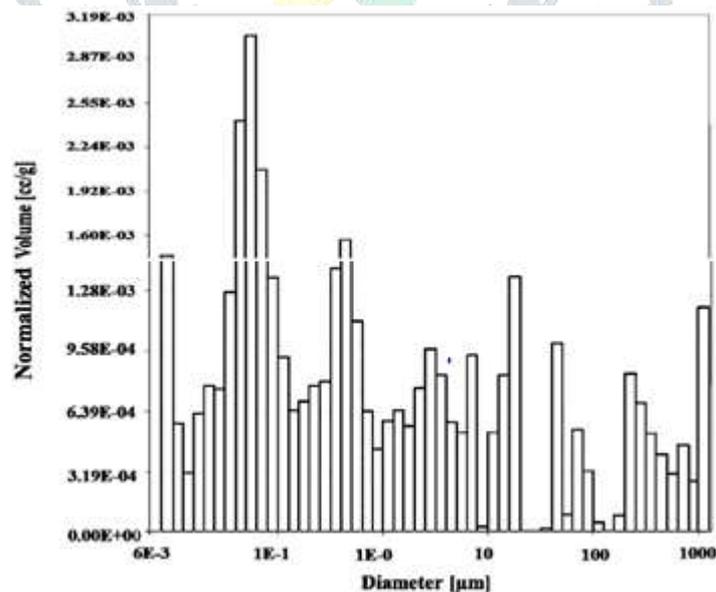


Fig. 7: Pore size distribution in the reference concrete

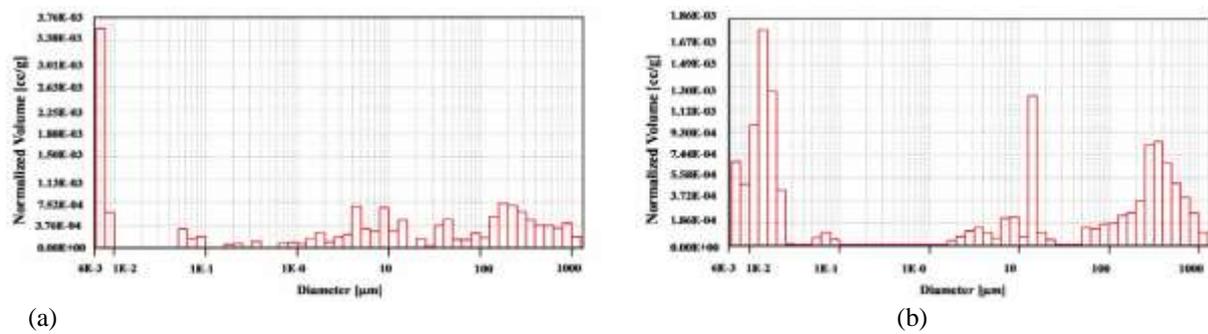


Fig. 8. Pore size distribution in concrete with different pozzolanic additives: a – micro/nanosilika, b – wood ashes

The result in Fig 8a, b compared with that of the reference concrete in Fig 7 shows a remarkable change in the pore distribution of concrete specimens after exposure to sulphate solution. It may be observed that pore volume and size increased for reference concrete specimens. This is due to aggressive action of sulphates on concrete arising from the destruction of the concrete structure. On the other hand it was observed that the total porosity of pozzolanic additives containing concrete, regardless of the solution (Na_2SO_4 or H_2SO_4) in all cases decreases. It is related to the ongoing processes of hydration and crystallization of salt in pores shown in Fig. 9. It can be seen that the concrete maturation process continues. Cementitious properties of pozzolanic materials and crystallization sulphate salt in pores decrease the number of pores in the range $0.5\text{-}10^3\text{ }\mu\text{m}$. The surface area of specimens has exposed corrosion process in depth up to 10mm.

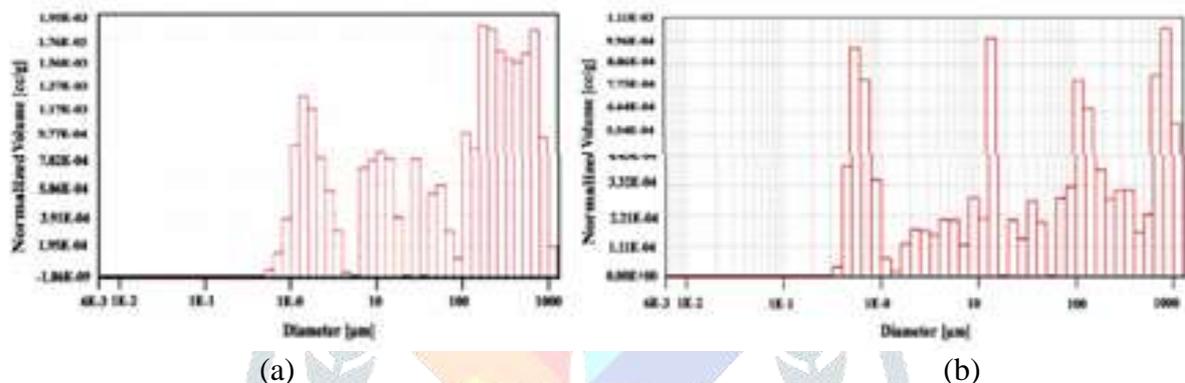


Fig. 9: Pore size distribution of concrete with different pozzolanic additives (a – micro/nano-silica, b – wood ashes) after exposure in H_2SO_4

The compressive strength of samples after exposure in sulphate solution remains at invariable value of 85-95MPa. The results showed that the addition of pozzolanic materials led to a high-strength concrete with very strong 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 (micro/nano-silica, wood ashes) activate the process of mineralization of concrete minerals such as tobermorite and hatrurite.

Finely dispersed pozzolanic additives were found to play a key role as micro fillers and supplementary cementitious materials resulting in the decrease of the number and size of pores. It was observed that the Reference concrete samples, when exposed to solution of sulphuric acid resulted in a heterogeneous structure with pores ranging from 10^{-3} to $10^3\text{ }\mu\text{m}$ in size. It was however discovered that with the addition of fine dispersed additives the number of large pores in the range between $1\text{-}10^3\text{ }\mu\text{m}$ decreased substantially.

After exposure of concrete with pozzolanic additives to SO_4^{2-} containing solutions, general crystalline phases remain unchanged for quartz and calcium silicates. Result also revealed that Gypsum was found on specimen's surface and extending down up to the depth of 10 mm. The results obtained in this study have shown that micro/nano-silica and wood ashes are 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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