



Effect of Micro Silica and Slag on the Durability Properties of Mortars against Accelerated Carbonation and Chloride Ions Attack

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ABSTRACT: Nowadays, as the cities grow, more carbon dioxide is emitted to the atmosphere moreover, chloride ions dissolved in water would reach the concrete whenever it rains consequently, they can help increase the corrosion of bars implemented inside concretes, therefore investigation of the effect of carbonation and chloride ingress is of paramount importance. Mortars were made with three water to cement ratios of 0.485, 0.44, and 0.4 also the flow of the mortars was kept in the range of 18 to 20 centimeters. The mixtures were prepared with ordinary Portland cement and artificial pozzolans (Ground Granular Blast Furnace Slag and Micro-Silica) as supplementary cementitious materials. The cement replacement percentage was 20% intended for slag-containing samples and 7.5% used for micro-silica-containing samples. The durability properties of mortars were investigated through capillary water absorption test, electrical resistivity, carbonation depth, and chloride ions penetration. Also, the mechanical characteristics of mortars were measured by the compressive strength test. The results revealed that Micro-silica enhanced the mechanical and durability properties of the specimens except for their resistance against carbonation, in both environments while, the addition of slag had some drawbacks in compressive strength and carbonation resistance. However, the addition of Slag helped specimens augment other durability properties. It can be concluded that using Micro-Silica is a magnificent option to enhance the mechanical and durability properties of mortars. The contribution of Slag has also been shown to help enhance the durability properties of mortars but not as much as Micro-Silica.

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1. INTRODUCTION

Concrete is doubtless one of the most consumed materials among construction materials in the world, while natural resources such as sand, gravel, water, and also energy in the shape of fossil fuels are used during the cement production process. Additionally, Portland cement production creates a large volume of CO₂ [1]. 2.8 billion tons of cement are produced annually and it is estimated to increase to 4 billion tons per year [2]. Thus, the need for decreasing the climate impact of the built-environment is substantial. One of the solutions to trim the environmental effects, mentioned above, is to increase material efficiency through the use of Decay of cement concrete occurs due to various reasons like chloride ingress, carbonation, sulfate attacks, etc. Furthermore, carbonation and chloride attack are more probable specifically in the urban and marine environment [3]. Industrial by-product which can be used as supplementary cementitious materials (SCM) [4]. Some of these supplementary cementitious materials are artificial pozzolans such as slag and micro silica. Ramezaniapour et al. reported that the addition of slag to the concrete decrease compressive strength at early ages (28 days) reversely silica fume increase [5].

The compressive strength of concrete mixtures containing micro silica doesn't increase significantly after the age of 90 days [6]. Grimaldi et al. found that in control mixtures, the depth of carbonation was higher than silica fume containing mortars. Therefore, they reported that this observation was because of pH reduction due to the pozzolanic reaction [7]. In higher w/b ratios, replacing cement with micro silica with a higher percentage leads to a higher depth of carbonation. Reversely in lower w/b ratios, it isn't predictable [8]. By adding slag to the concrete, the electricity resistivity will be increased in all age and w/b ratios [9]. Researches showed that carbonation increases the electrical resistivity of concrete [10]. Also, carbonation causes decreasing concrete porosity. Ramezaniapour et al. reported that the use of slag leads to decreasing in porosity which causes increasing the electricity resistivity [9]. By keeping the replacement of silica fume at the level of 10% (by weight), Gonen and Yazicioglu investigated the effect of adding mineral admixtures on capillary water absorption of the concrete. They reported that mineral admixtures caused capillary pore refinement in both cement matrix pores and pores located in the transition zone [11]. The effect of silica fume on refining the porosity

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of the mortar was evaluated by Gleize et al. The replacement of silica fume was considered 10% (by cement weight). They showed that after 28 days, the porosity of the micro silica containing mortars was lower in comparison to the control mortars. Also, the pore structure of the pozzolanic mortars seemed to be finer. However, the pore size refinement was more significant at 28 days than 2 days due to the pozzolanic reaction of silica fume [12]. The capillary porosity and pore size distribution of high-strength concrete (HSC) with 10% silica fume as supplementary cementitious material was investigated by Igarashi et al. at their early ages. According to their results, control specimens in comparison to silica fume-containing concrete were observed to have coarser pores, even at early ages of 12 and 24 h. The diameter after which the porosity experienced a dramatic augment with decreasing pore diameter showed to be bigger in control specimens at 12 h [13]. Poon et al. studied the specimens' porosity with the MIP test. Specimens were made with w/b ratios of 0.3 and 0.5 with silica fume replacement of 10 and 15 percent (by cement weight). The results showed that by adding silica fume to the specimens, the porosity of the pozzolanic concretes decreases with age [14]. It is also stated that adding silica fume to the mixture can considerably reduce the specimen's permeability and diffusion of chloride ion since pozzolanic reactions of silica fume entail pore refinement by turning bigger capillary pores into small ones. [15]. The chloride resistance of mixtures containing both fly ash and silica fume were compared to Portland cement in Ozyildirim and Halstead's study and the pozzolanic mixtures proved to have a better chloride resistance [16]. shekarchi Zadeh et al. studied on chloride diffusion of concrete with 5,7.5,10 and 12.5 percent replacement of silica fume in the Persian Gulf environment. They reported chloride diffusion decreases by passing time and 7.5 percent of replacement is optimum [17]. Replacement of micro silica more than 10 percent doesn't improve chloride diffusion especially [18]. Probes have been considered the effect of pozzolans on the resistance of concretes against carbonation and chloride attack. Although using pozzolans reduces the porosity of concrete and prevents chloride ingress, it reduces the concrete resistance against carbonation. Hence the overcoming phenomena are unexplored. According to J. Liu et al. carbonation increases the chloride ion penetration, however, in the presence of chloride ions, carbonation decreases in concrete containing fly ash. The simultaneous effect of chloride ions and carbonation leads to the denser microstructure of concrete and increases the proportion of small holes in concrete containing ash. (In comparison with chloride ion or carbonation lonely) [19].

In this research, the effect of Slag and Micro silica addition, as artificial pozzolans (SCM), on the durability properties of mortars is scrutinized. Also, the effect of carbonation on the water absorption and surface electrical resistivity of the mortars is probed.

2. EXPERIMENTAL PROGRAM

2.1. Materials

The primary binder utilized in this study was the type

I-425 Portland cement meeting the ASTM C150 requirements moreover, slag (S) and Micro-silica (MS) were applied as supplementary cementitious materials (SCM). Physical properties and chemical analysis of cement and other pozzolanic materials are listed in Table 1. Binders' particle size distribution is shown in Fig.1. Also, the pozzolanic reactivity of micro silica and slag is shown in Table 2. River sand meeting the requirements of ASTM C33 (see Table 3) with a density of 2.56 gr/cm³ and water absorption of 2.9% was used. Additionally, a polycarboxylate ether-based superplasticizer (SP) was necessary to achieve the desired workability. Potable water was used for both mixing and curing purposes.

2.2. Mixture design

Nine mortar mixtures were built with three different water proportions in mixture design. The water to binder (W/B) ratios applied to mixtures are 0.485, 0.44 and, 0.4. Test specimens were braced with 20% and also 7.5% (by weight) replacement of cement with Slag and Micro silica respectively. The mixture proportions are presented in Table 4. In concrete mixtures with a constant slump of 100±10 mm, those incorporating higher silica fume replacement levels tended to require more dosages of superplasticizer [6]. The flow rate of the mortars was kept constant in the range of 18-20 cm using an appropriate amount of superplasticizer unless the mortar's flow rate was more than the specified range which is identified with an asterisk in Table 4. After casting, specimens were covered for 24 hours to prevent excessive water loss due to evaporation. They were then de-molded and cured for 56 days in calcium hydroxide-saturated water at 23±2 °C to prevent possible leaching of Ca(OH)₂ from these specimens.

3. RESULTS AND DISCUSSION

3.1. Compressive strength

For each mix design, mortar specimen cubes of 100×100×100 mm dimension were cast for measuring compressive strength. Compressive strength is an index of mechanical properties. This test has been done according to ASTM C39. As can be seen in Fig.2, the compressive strength increases as the w/b decreases in all the specimens. Ramezani pour et al. reported that the addition of local slag has a negative effect on compressive strength, while silica fume improves the strength value, especially at 28 days [20]. Yajun et al. concluded that silica fume improves compressive strength until late ages (90 days) [21]. The addition of artificial pozzolans has decreased the compressive strength of mortars containing Slag. The reason for this reduction in slag-containing mortars could be related to the low pozzolanic reactivity of slag. As it is illustrated in Fig.2, slag mortars have not reached the control specimens' compressive strength until 90 days. From the beginning, Micro silica-containing mortars possessed a compressive strength more than that of control specimens. It could be related to the high content of SiO₂ in Micro Silica's structure leads to a high pozzolanic reaction.

Table 1. Chemical and physical properties of binders.

Chemical composition	Portland Cement I-425 (%)	Slag (%)	Micro silica (%)
SiO ₂	20.8	36.6	92.8
Al ₂ O ₃	3.09	7	0.39
Fe ₂ O ₃	5.6	0.55	1.24
CaO	63	40.9	0.7
MgO	1.36	6.4	0.57
SO ₃	-	0.19	0.13
Na ₂ O	0.20	0.28	0.2
K ₂ O	0.80	1.14	0.69
LOI	2.19	0	2.97
Physical properties	Portland Cement I-425	Slag	Micro silica
Specific gravity (gr/cm ³)	3.09	2.86	2.16
Fineness (Blaine) (cm ² /gr)	3299	3715	19998

Table 2. pozzolanic reactivity of slag and micro silica.

mixture	7 days compressive strength (Mpa)	28 days compressive strength (Mpa)	7 days pozzolanic reactivity (%)	28 days pozzolanic reactivity (%)
cement mixture	34.6	49.6	-	-
slag mixture	31.2	40.6	90	90
micro silica mixture	36	56.6	104	125

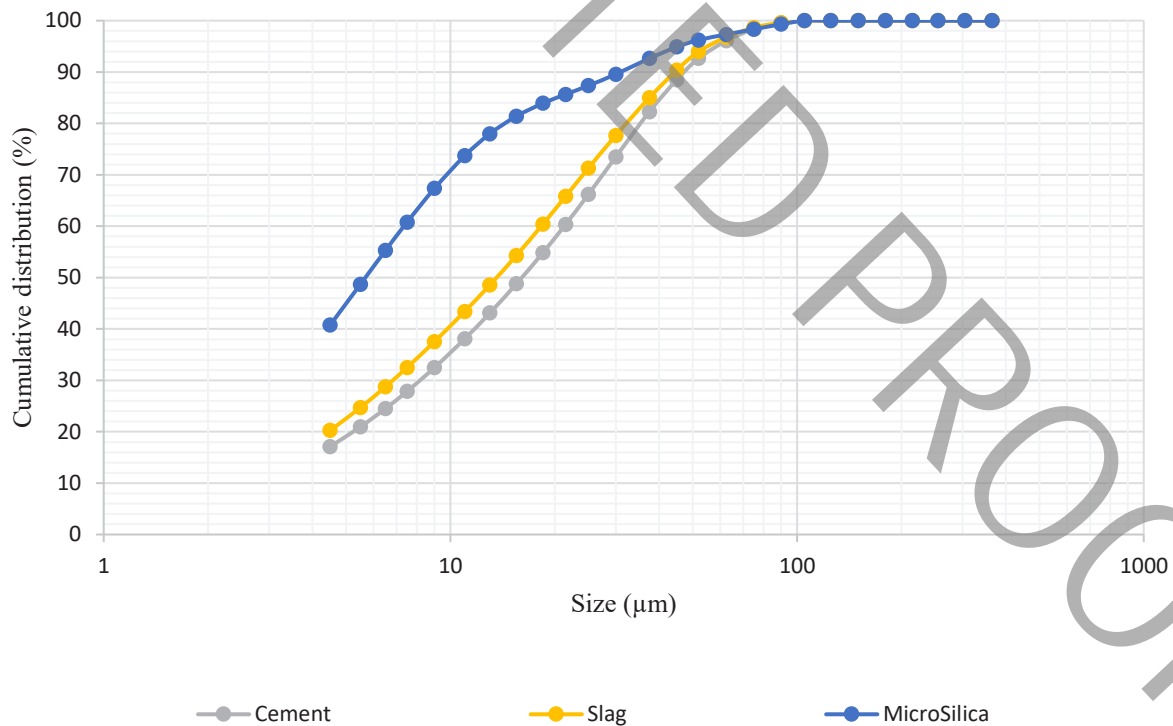


Fig. 1. Binders' particle size distribution.

Table 3. Graded sand according to ASTM C33.

sieve	Sieve size	Passing Sieve (%)	
		ASTM C33	Experimental program
3/8 in	9.51 mm	100	100
No. 4	4.76 mm	95-100	95.3
No. 8	2.38 mm	80-100	81.8
No. 16	1.19 mm	50-85	51.3
No. 30	595 μ m	25-60	32.4
No. 50	297 μ m	5-30	12
No. 100	149 μ m	0-10	2.4

Table 4. Mixture design of the mortars.

Mixture ID	W/B	Cement (kg/m ³)	Pozzolan (kg/m ³)	Water (kg/m ³)	Sand (kg/m ³)	SP/B
C-0.485*	0.485	520	0	252.2	1431	0
C-0.44	0.44	520	0	228.8	1491	0
C-0.4	0.4	520	0	208	1544	0.24
S-0.485	0.485	416	104	252.2	1422	0
S-0.44	0.44	416	104	228.8	1482	0
S-0.4	0.4	416	104	208	1533	0.197
MS-0.485	0.485	481	39	252.2	1416	0.15
MS-0.44	0.44	481	39	228.8	1475	0.27
MS-0.4	0.4	481	39	208	1526	0.42

3.2. Carbonation depth

The carbonation depth of three specimens was measured after 63, 105, and 147 days of exposure to CO₂ gas in the carbonation chamber in addition to 56 days of curing for each mixture, and the results are demonstrated in Fig.3. Specimens were disk-shaped with 100 mm diameter and 50 mm length with all their faces except one coated with a substance preventing CO₂ ingress.

It can be observed that carbonation depth increases with the increase of CO₂ exposure duration for all selected w/b and pozzolans. It is also illustrated that with a decrease in w/b, the carbonation resistance of the mortars with and without pozzolans has increased. The lower w/b leads to improve the microstructure of matrix paste that decreases porosity and increases the CO₂ ingress resistance. The results further show that the addition of artificial pozzolans increases the carbonation depth of the mortars except in MS-0.4. This can make them more vulnerable to carbonation attacks. Diamond reported that using fly ash in concrete decreases the PH value of the pore solution [22]. Ramezainpour explained pozzolans consume calcium hydroxide as the progress of the pozzolanic reaction which leads to a reduction in PH of pore solutions [23]. In MS-0.4 the reduction of porosity due to high pozzolanic reactions was more effective than the reduction

of pH which makes it's more resistant against CO₂ ingress.

3.3. Absorptivity

The rate of water absorption is measured according to ASTM C1585. To do so, three mortar disks of 100 mm diameter and 50 mm length were obtained from molded cylinders according to ASTM C31/C31M for each mixture and were cured in the noted conditions then, all the surfaces of the specimens except one which was submerged in water for 2 \pm 1 mm were covered by impenetrable tape to prevent any water absorption from other sides. Finally, the weight of absorbed water was measured in the recommended intervals and the mean value was reported.

The results of the initial and secondary rates of water absorption are illustrated in Fig. 4 and Fig.5, respectively. It can be understood from Fig. 5 that the addition of artificial pozzolans has contributed to the reduction of mortar's initial rate of water absorption in all ages while in the case of the secondary rate of water absorption slag containing mortars have more absorption than control specimen in all ages but in Micro Silica containing mortars is reverse.

As the w/b decreases, because of lower porosity, the initial rate of absorption decreases. However, it can be reported that the fewer the w/b, the fewer the secondary rate of absorption

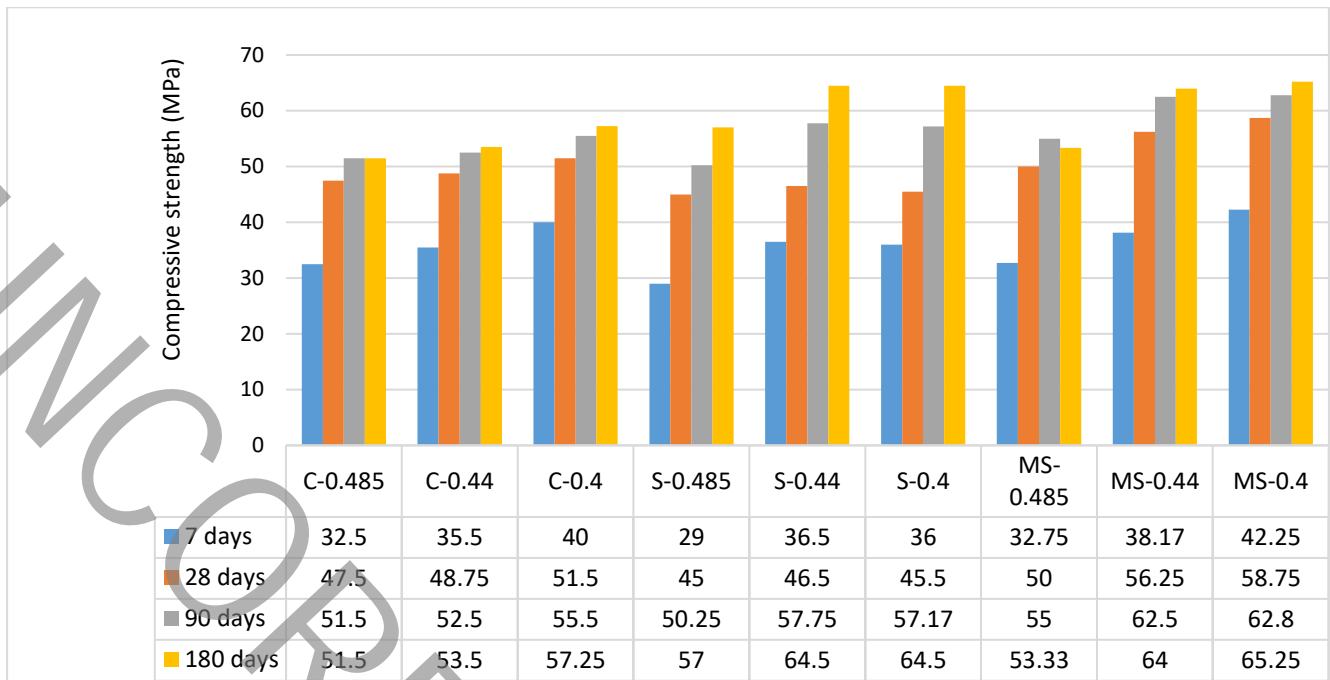


Fig. 2. Compressive strength of the mortars.

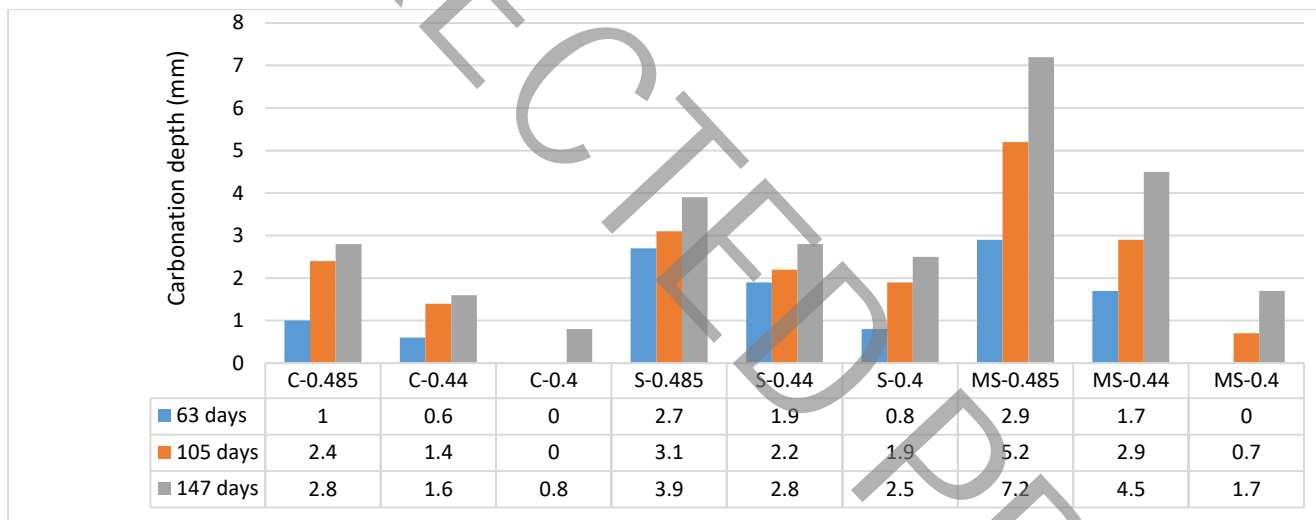


Fig. 3. Carbonation depth of the mortars.

in each pozzolanic mortar.

To investigate the effect of carbonation on the mortar's capillary water absorption, the same test was done on specimens that were initially cured for 56 days in water and kept in a carbonation environment for 63, 105, and 147 days. The results are demonstrated in Fig. 6 and 7.

In the control mortars, the initial rate of water absorption has decreased because of a decrease in capillary porosity

due to the reaction of CO_2 and calcium hydroxide and consequently the formation of calcium carbonate. This observation is in agreement with a previous study [24].

As it is depicted in fig,6, no clear trend in slag-containing and micro silica-containing mortars was seen. This can be related to the obscure effect of carbonation on the porosity and microstructure of the mortar's matrix. In slag containing

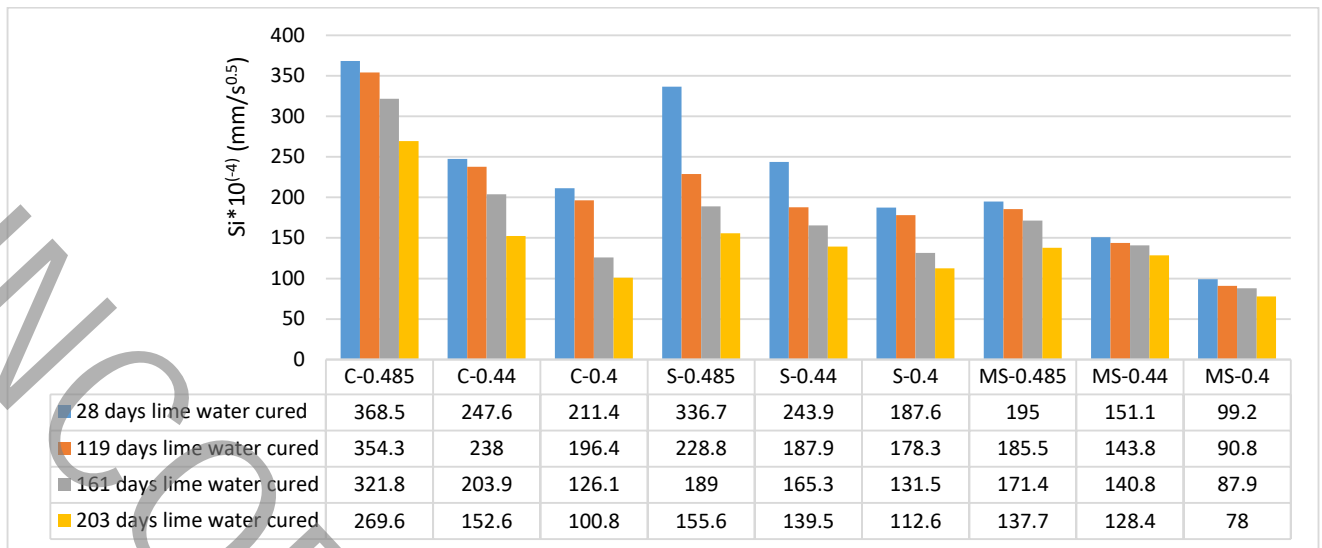


Fig. 4. Initial rate of water absorption of the mortars cured in lime water.

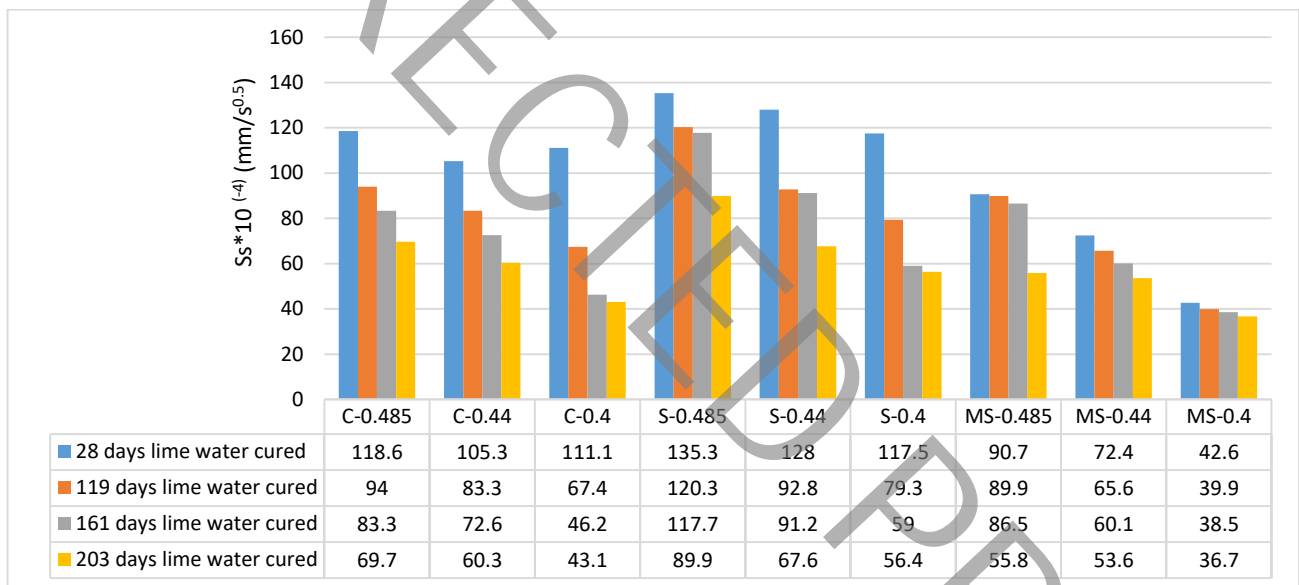


Fig. 5. Secondary rate of water absorption of the mortars cured in lime water.

mortars, the initial rate of water absorption was increased but the secondary rate of water absorption was increased. In Micro Silica containing mortars both initial and secondary water absorption rate increases. According to Wu & Ye, carbonation has increased the total and effective capillary porosity of a pozzolanic concrete [25]. On the other hand, Hussain, Bhunia & Singh have reported a reduction in the pozzolanic concrete's porosity [26].

3.4. Surface electrical resistivity

The electrical resistivity test was conducted using the Wenner four-probe method according to AASHTO T358. Three lime water-saturated 100×200 mm cylindrical specimens were tested for each mix design. The outcome is a function of moisture and electrolyte content of the pores, therefore, consistency of the tested specimens' moisture is of paramount significance to reach an acceptable result [27]. Consequently, to test the specimens which were kept in the

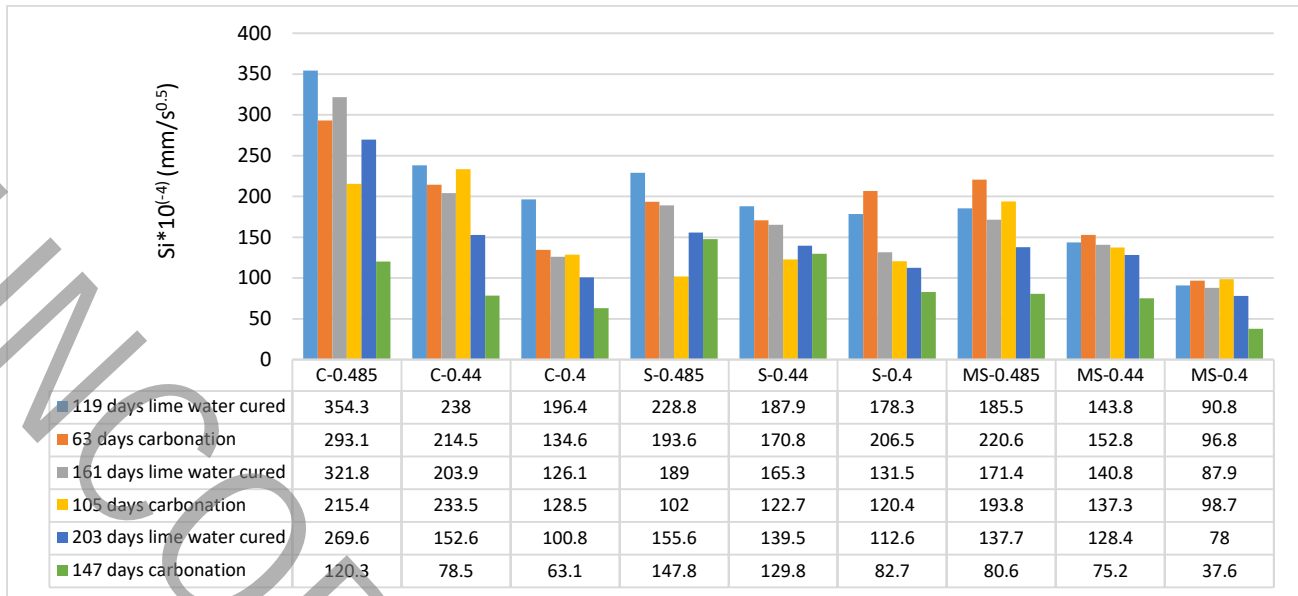


Fig. 6. Effect of carbonation on the initial rate of water absorption.

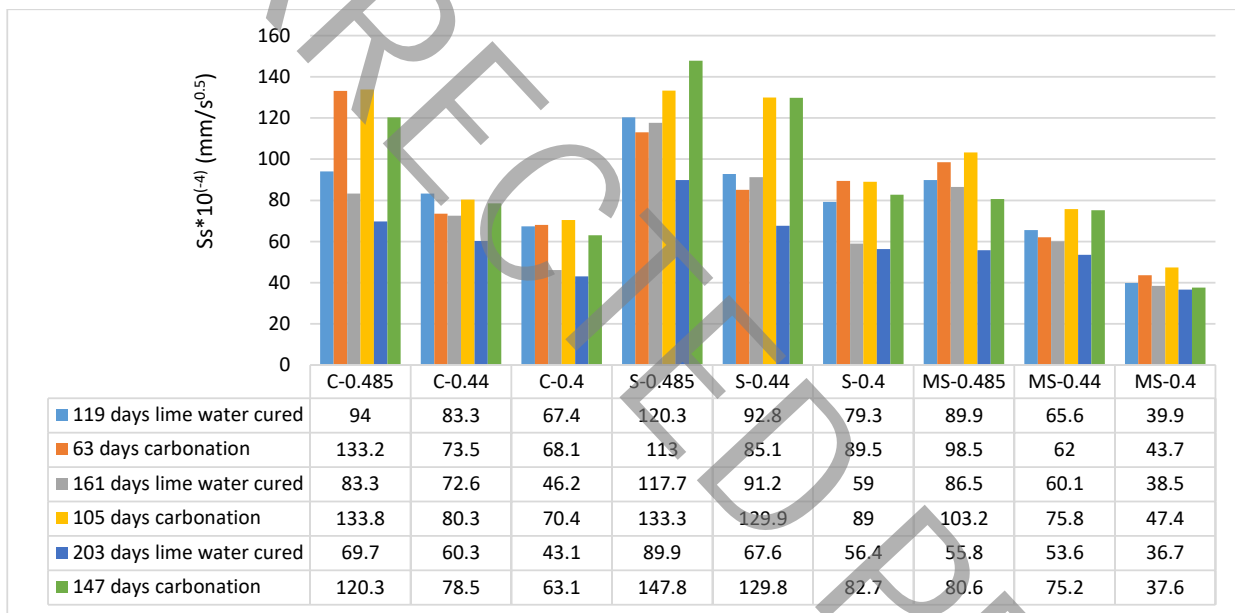


Fig. 7. Effect of carbonation on the initial rate of water absorption.

carbonation chamber, they were maintained in water for 7 days to become saturated.

The results of electrical resistivity at 56, 119, and 161 days are shown in Fig. 8. It is observed that by decreasing the w/b ratio, the electrical resistivity of specimens increases as a result of a denser matrix.

The effect of slag and Micro Silica addition in all ages improved the electrical resistivity of specimens because of the formation of secondary C-S-H gel due to pozzolanic reactions. It is worth mentioning that the addition of Micro

Silica hugely contributes to the enhancement of electrical resistivity of specimens even after 56 days which proves the formerly mentioned note that Micro Silica benefits from a higher pozzolanic reactivity in comparison to slag. As it is depicted in figure 8 the MS-0.4 mixture has a relatively high electrical resistivity because of its very dense matrix, as mentioned before.

It is noteworthy that the difference of electrical resistivity values between 56 days and 161 days is higher in lower w/b for both slag and micro-silica containing mortars which

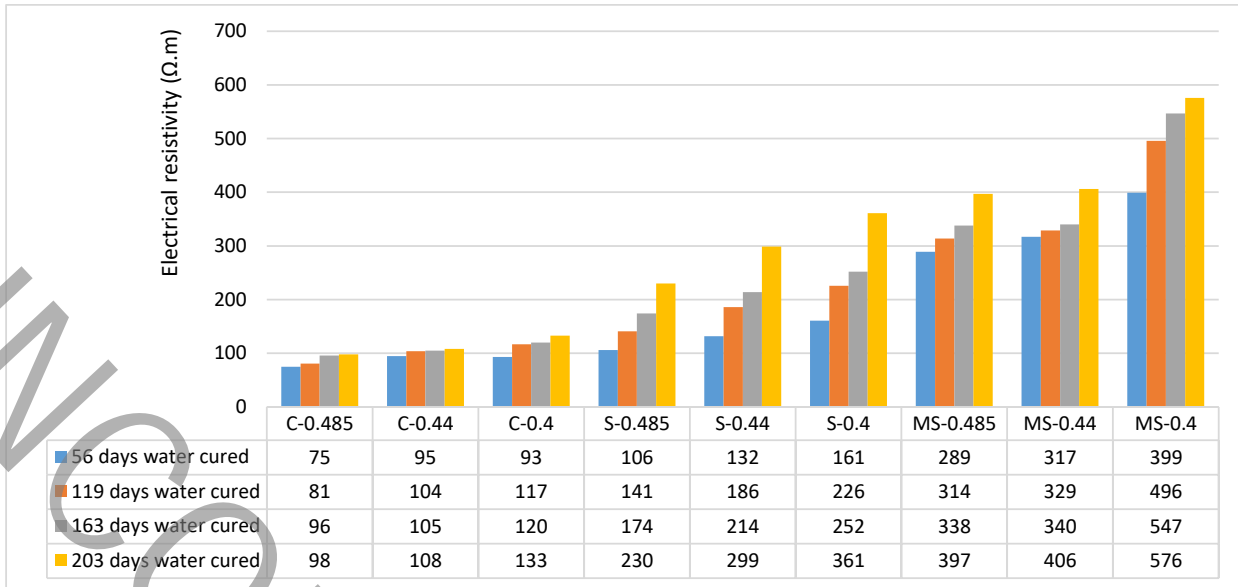


Fig. 8. Electrical resistivity of the mortars

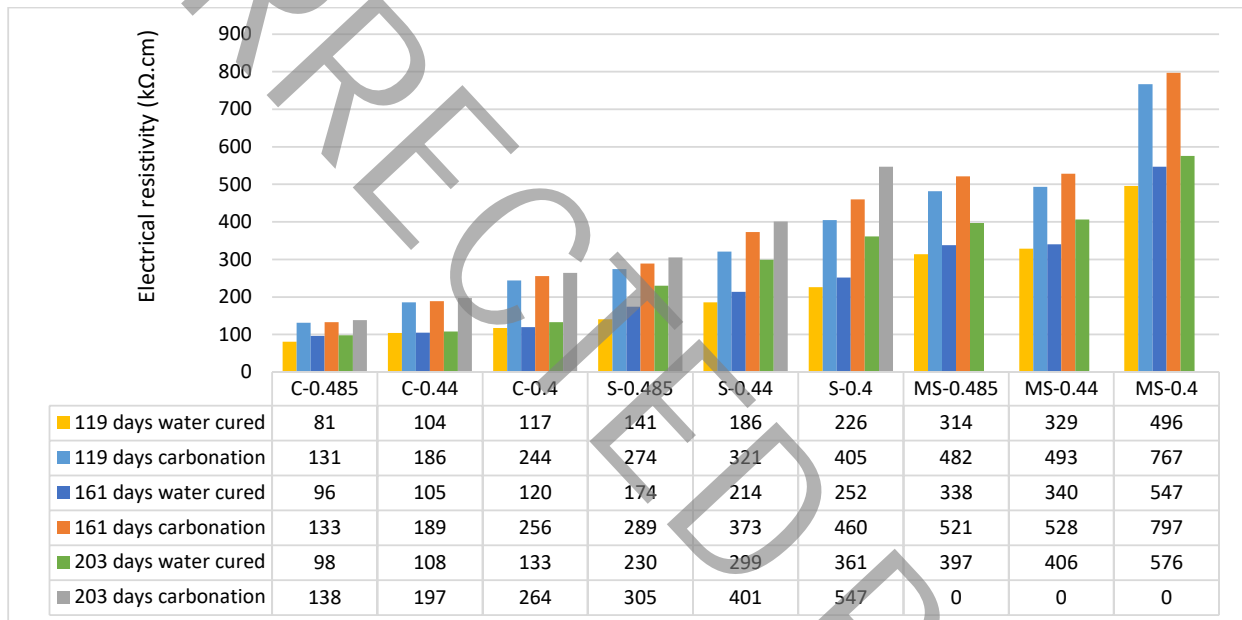


Fig. 9. Effect of carbonation on the electrical resistivity of the mortars

reveals that pozzolans show better performance when used in lower w/b.

The effect of carbonation on the electrical resistivity of mortars is measured and shown in Fig.9. To do so, specimens were kept in the carbonation chamber for 63,105 and 147 days after 56 days of water curing in lime-water. It has been observed that carbonation increases the electrical resistivity of mortars even if the carbonation depth is negligible. It can be explained that carbonation reduces the pH value of matrix fluid of the mortars through consumption of $\text{Ca}(\text{OH})_2$ content

due to its reaction with CO_2 which seems to be the prevailing factor on grounds that the other factor, which is the reduction of capillary pores, is not quite relevant as it is mentioned in former sections. It can be seen that the difference of electrical resistivity value of carbonated and water cured specimens increase by the reduction of w/b, although their carbonation depth decrease which holds the effect of alkalinity reduction of matrix fluid. It can be concluded from Fig.9 that the increase of electrical resistivity of mortars exposed to CO_2 in mortars with lower w/b outperforms other w/b. This means

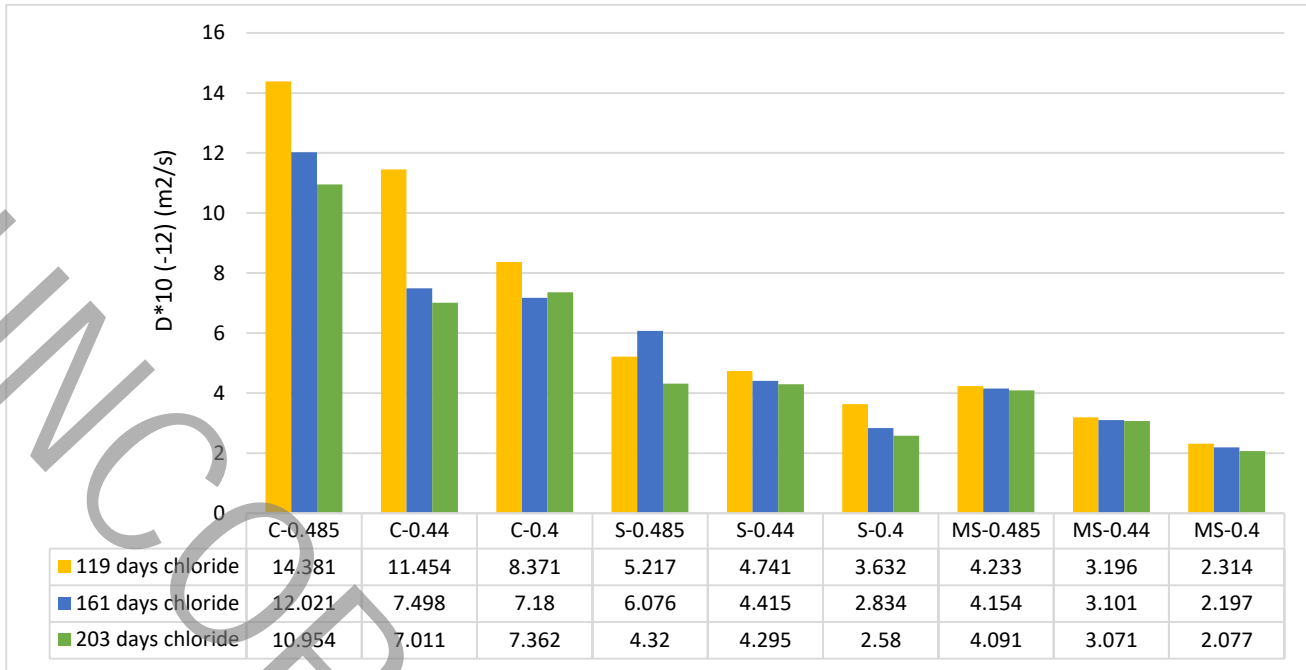


Fig. 10. Diffusion coefficient of the specimens.

that pozzolans have a better performance in lower w/b. micro silica-containing mortars were showed higher electrical resistivity than slag-containing mortars. It can be related to the high pozzolanic reactivity of micro silica due to the high content of SiO₂ which leads to a denser paste matrix.

3.5. Chloride bulk diffusion

The mortar's chloride bulk diffusion is measured according to NT Build 443 through 100 × 100 × 100 mm cubical specimens after 119, 161, 203 days for each mix design to directly indicate the chloride resistance of the mortars. The results are shown in Fig.10. It can be observed that the lesser the water to binder ratio, the lesser the chloride diffusion coefficient which can be related to a denser matrix enhancing the transport properties of the mortars. As demonstrated in figure 10. Chloride diffusion decreases whit increasing the age of the specimen. It can be related to the improvement of pore structure due to C-S-H formation by the time. Ramezaniapour et al. reported that the addition of a 7.5% silica fume causes a remarkable reduction in chloride diffusion into concrete [15]. Tests show that low-reactivity slag can improve the chloride resistance of concrete mixtures by the age of 180 days [28]. The pozzolanic mortars show a remarkable reduction in their diffusion coefficient due to pore refinement which is entailed by the pozzolanic reactivity. Moreover, Micro Silica has shown to be a better choice in decreasing the diffusion coefficient.

4. CONCLUSIONS

In this paper, the effect of the addition of Micro Silica and slag on the durability properties of mortars exposed

to accelerated carbonation and chloride ingress has been investigated. According to the results, the following conclusions could be reported.

By lowering the w/b, the mechanical and durability properties of mortars enhance due to the generation of a denser matrix.

The Slag-containing mortars due to the relatively few silica contents in comparison to Micro Silica containing mortars do not evince a noteworthy pozzolanic reaction at in early ages, however, in the later ages, Slag proves to be useful in increasing both mechanical and durability properties of mortars, except in carbonation resistance.

The Micro Silica containing mortars showed great durability properties which can be related to high SiO₂ content.

Consumption of Ca(OH)₂ due to the addition of artificial pozzolans reduces the matrix pH which makes them more vulnerable to carbonation.

Carbonation decreases the initial and secondary rate of water absorption in control mixtures because of calcium carbonate generation which decreases the porosity of the mortars. Whereas, it cannot be clearly explained the effect of carbonation on the water absorption rate of pozzolanic mortars due to the inconsistent effect of carbonation on the total and capillary porosity of pozzolanic specimens.

The electrical resistivity of the mortars cured in the carbon dioxide environment has been increased in comparison to mortars cured in water even for specimens with negligible carbonation depth.

The use of micro silica and slag can decrease the chloride diffusion coefficient. It can be related to pozzolanic reactivity and paste matrix refinement.

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