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Investigating the synergistic effect of Nano and Micro silica on porosity of cement mortar by FE-SEM image analysis

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***Abstract*- In recent years combined usage of the supplementary cementitious materials especially Ns and MS has become a popular topic. The aim of this study is to investigate the synergistic effect of nano- and micro-silica on the porosity of the cement mortar by using FE-SEM images. Therefore, 12 mix designs with different amounts of nano- and micro-silica with two W/B ratios have been considered. Also, FE-SEM images were taken from the control specimen, and the best mixtures in the form of Ns alone, Ms alone, and combined Ns and Ms. Consequently, a comparative investigation was carried out to evaluate the effect of different percentages of nano- and micro-silica on the porosity and microstructure of cement mortar. The results show that the addition of nano- and micro-silica gradually decrease porosity and improves the microstructure of the specimens. nevertheless, simultaneously usage of them leads to the lowest porosity values and the most compact microstructure. Also, The microstructure observations have been confirmed the experimental porosity results.**

***Keywords* –**Cement mortar, Nano silica, Micro silica, Porosity, Microstructure

1. INTRODUCTION

Over the past decades, in mortar or concrete mixtures cement has been replaced with cementitious or pozzolanic materials in order to improve mechanical properties and microstructure [1–3]. In this regard, nano-silica [4], micro silica [5], fly ash [6], metakaolin [7] and etc. have been extensively used as supplementary cementitious materials. For instance, due to pozzolanic reactivity and chemical compositions of fly ash as supplementary cementitious material, the compressive strength of the mortar would improve [8]. Another high reactive pozzolanic material is metakaolin which has been successfully added to the mortar mixtures and leads to improvement in compressive strength and sulfate resistance [7]. Furthermore, the materials with finer size than cement particles such as micro silica are more effective [9]. The high reactivity of them is due to the large surface area and also they could fill the voids because of their fine size [10]. The effect of adding Ms has been widely investigated and showed that it can improve the mechanical properties and microstructure of the cement-based materials [11]. For example, Perraton et al. [12] observed that Ms has significantly reduced the chloride ion permeability as a result of pore refinement by adding Ms. In another study the pore structure of the silica fume concrete investigated and demonstrate that higher amount of silica fume leads to lower porosity and average pore size [2].

By the development in nanotechnology, nanomaterials with finer size than Ms become known and used more in the cementitious materials [13]. Many pieces of research have been investigated the effect of adding various nanoparticles as supplementary cementitious materials. As an example, nano-$CaCO_3$ [14] improves the microstructure and strength of concrete. Other investigations have been studied the effect of nano-TiO_2, nano-Fe_3O_4 , and nano clay on microstructure, mechanical properties, and durability of cement-based materials [15–17]. Due to the high pozzolanic reactivity and ultrahigh fineness of nano-silica, more attention has been attracted to Ns as additives to cement-based materials [18].

In recent years combined usage of the supplementary cementitious materials especially Ns and MS has become a popular topic [2,9,19]. In cement-based materials, MS fills the void between cement grains and Ns which is finer particle would fill the void between Ms particles. Due to this fact, a more compact structure would be formed so the microstructure and performance of the mortar and concrete would improve. For instance, the effect of adding Ms and Ns to the concrete studied and showed that the combination of 10%Ms and 2%Ns lead to the highest compressive strength and lowest chloride penetration of the concrete [20]. Sharkawi et al. [21] investigated the effect of adding Ms and Ns on the durability performance of the cement-based materials and revealed that blending of 8%Ms+2%Ns leads to most increment in compressive strength and remarkably improve the durability performance . In 2017, Li et al. [19] investigated the synergistic effect of the Ms and Ns on the durability of the mortar and noted that the presence of Ms and Ns simultaneously would improve the chloride, sulfate, carbonation, and water resistance of the cement mortar. The synergistic effect of the Ns and Ms on the microstructure of the cement mortar has been studied by li et al. in 2017 [2]. They have been indicated that blended usage of Ns and Ms has a synergistic and more significant effect on densifying the microstructure of mortar in comparison to using them alone.

The aim of this study is to investigate the synergistic effect of Ns and Ms on porosity and microstructure of cement mortar. Therefore, several mixtures with different Ns and Ms contents were produced to calculate the porosity of specimens and microstructure analysis. A comparative evaluation of the effect of adding Ns alone, Ms alone, and blended Ns and Ms on porosity and microstructure of the specimens have been done based on the experimental results.

2. Experimental Program

2.1 Materials

Three main ingredients of the cement mortar are cement, aggregates and water. Portland cement with 32.5 MPa strength class and various amounts of Ns and Ms were selected for the preparation of mix designs. The chemical and physical properties of cement, nano and micro silica are shown in Table 1. High range water reducing (HRWR) based on carboxylic ether polymer has been used to improve the workability of the mixtures. The maximum particle size of the sand aggregates and fineness module was 4.75 mm and 2.6, respectively. The particle-size distribution curve of aggregates in accordance with ASTM C778 [22] is represented in Fig. 1.

Table 1. Chemical and physical properties of cement, Nano and Micro silica.

Properties	Variable	CEM 32.5	Ms	Ns
Chemical Analysis (%)	SiO_2	20.89	89.6	23.6
	Al_2O_3	4.21	-	0.13
	Fe_2O_3	3.80	-	0.07
	CaO	64.21	-	0.07
	MgO	1.94	-	0.05
	SO_3	2.4	-	0.1
	Na_2O	0.31	0.11	9.2
	K_2O	0.67	0.3	0.12
	LOI	2	3.8	-
	FCaO	1	-	-
	C_3A	4.73	-	-
	C_3S	62.07	-	-
Physical Analysis	Density (gr/cm^3)	3.183	1.9	1.2
	Sieve residue on 90 mm (%)	0.6	-	-
	Blaine Test(cm^2/gr)	3467	22000	-

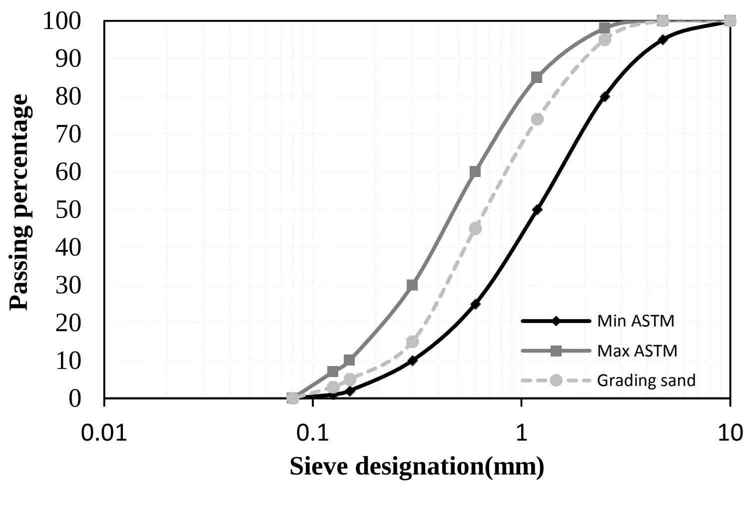

Fig 1. Grading curve of sand aggregate.

2.2 Mixture proportions

An experimental plan was developed to investigate the effect of various amounts of Ns and Ms on porosity. In this study, 0.4 and 0.5 are the used W/B ratios while the amounts of Ms are 0%, 9%, and 13%, and also the Ns amounts are 0%, 2.8%, and 4.2%. The proportions of 12 mix designs are presented in Table 2. The HRWR amounts discovered through the mixing procedure by gradually adding until gaining at least 120±5 mm flow spread. Cubic specimens with 50 mm^3 dimensions were used. All the specimens were cut from the mold after 24h and then cured in the water for 28 days.

With a view to measure the porosity of specimens at the age of 28-days, saturated surface dry (Wssd), water immersed (Ww) and dried specimens weight have been measured. Consequently, the following equation has been used to calculate the porosity:

$$P = \frac{W_{ssd} - W_d}{W_{ssd} - W_w} \times 100 \tag{1}$$

Where P is the percentage of porosity. It is worth noting that this method has been successfully utilized in other investigations [23].

Table 2. Mix proportions of cement mortar specimens.

Mix ID	C (gr)	W/C	S/C	Ns/B	Ms/B	W/B	HRWR (ml)
NMsi-0/0	1200	0.500	2.667	0	0	0.50	4
NMsi-0/9	1092	0.549	2.930	0	9	0.50	11.6
NMsi-0/13	1044	0.575	3.065	0	13	0.50	14.5
NMsi-2.8/0	1166.4	0.514	2.743	2.8	0	0.50	7.5
NMsi-4.2/0	1149.3	0.522	2.784	4.2	0	0.50	9
NMsi-2.8/9	1058.4	0.567	3.023	2.8	9	0.50	13.5
NMsi-0/0	1200	0.400	2.667	0	0	0.40	5
NMsi-0/9	1092	0.440	2.930	0	9	0.40	14
NMsi-0/13	1044	0.460	3.065	0	13	0.40	17.5
NMsi-2.8/0	1166.4	0.412	2.743	2.8	0	0.40	9
NMsi-4.2/0	1149.3	0.418	2.784	4.2	0	0.40	11
NMsi-2.8/9	1058.4	0.454	3.023	2.8	9	0.40	16

*C = Cement, W/C = Water to Cement ratio, S/C = Sand to Cement ratio, Ns/B = Nano silica to Binder ratio, Ms/B = Micro silica to Binder ratio, and HRWR= High range water reducer.

2.3 FE-SEM analysis

In order to investigate the effect of Ns and Ms on the microstructure of the cement mortar, SEM images were taken by a field emission scanning electron microscope (FE-SEM) from small mortar samples with a volume of less than 1 cm^3. In this regard, small particles were cut from virgin specimens that cured for 28 days and then soaked in ethanol for over 7 days to stop the chemical reactions. The Hitachi-S-4160 apparatus was used for image scanning in 1000X magnification.

3. Results

3.1 Porosity

The experimental results of porosity at the age of 28 days versus Ns and MS content values for 12 mix designs with 0.5 and 0.4 W/B ratios are shown in Fig. 2. It can be observed from fig.2 that in both W/B ratios adding Ms alone up to 9% and Ns alone up to 4.8% gradually decreases the porosity of the mortar specimens. In this regard, it is worthy to note that the addition of 2.8% Ns alone decreased the porosity values more than adding 9% Ms alone. Furthermore, it clearly illustrated that the combined addition of Ns and Ms has a more significant effect on decreasing the porosity of the cement mortar specimens.

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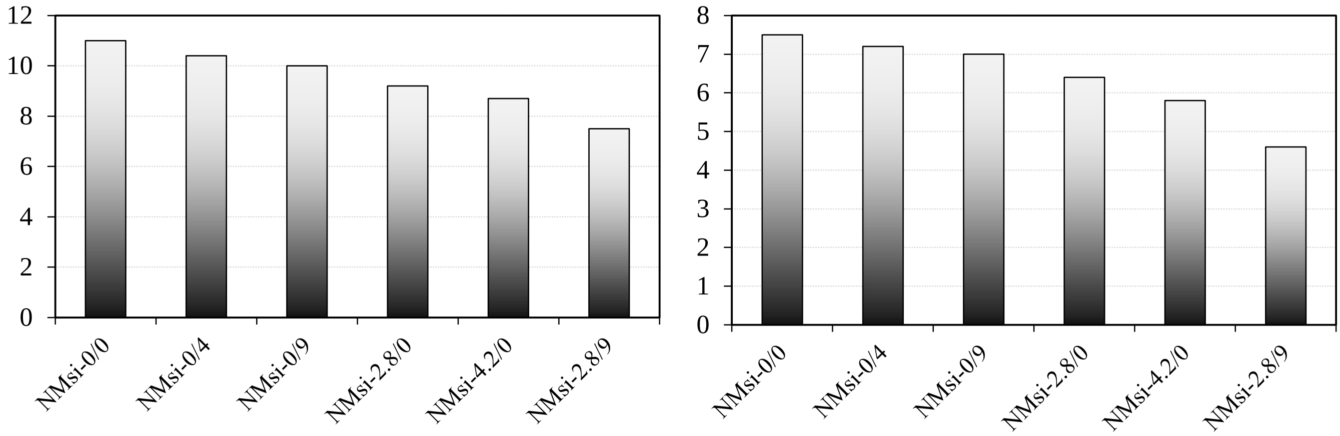

Fig 2. Porosity of each mixture.

3.2 SEM image analysis

The surface microstructure FE-SEM images and the porosity presentation of cement mortar specimens comprise of 0% Ms+0% Ns, 9% Ms+0% Ns, 0% Ms+4.2% Ns, and 9% Ms+2.8% Ns at W/B of 0.50 and 0.40 and are depicted in Figs 3 and 4 respectively. According to the mentioned figures, huge crystals, numerous void and consequently poor microstructure could be seen in the FE-SEM images of control mortar which significantly decreased by adding Ms and Ns to the mixtures. Furthermore, using Ms or Ns alone decrease the number of pores, forms a more dense structure and in general, improves the microstructure of the specimens but the FE-SEM images still indicate some enormous crystal. It is necessary to note that the Ns has a larger surface area so, the lower values of Ns have more efficient influence than Ms values in the mixture. For instance, the specimens comprising of mere 4.2%Ns have a better modification effect in comparison with specimens comprising of mere 13% Ms. Moreover, it is obvious from Figs. 3d and 4d that the simultaneous use of Ms and Ns contents in the mixture leads to a significant reduction in the number of formed large crystals and eventually a dense compact structure have been formed. Also, as Figs. 3 and 4 shows, the density of the specimens with W/B of 0.50 was lower than that of the similar mixture with W/B of 0.40. These microstructure observations indicate that the synergistic effects of the simultaneous presence of Ms and Ns contents in the hardened mortar specimens lead to a dense microstructure, filled pore structures, and ultimately, provoke higher amount of C–S–H gel and CH. Besides, these observations are in agreement with the experimental porosity results in section 3.1 which showed that using simultaneously Ns and Ms has lowest porosity values.

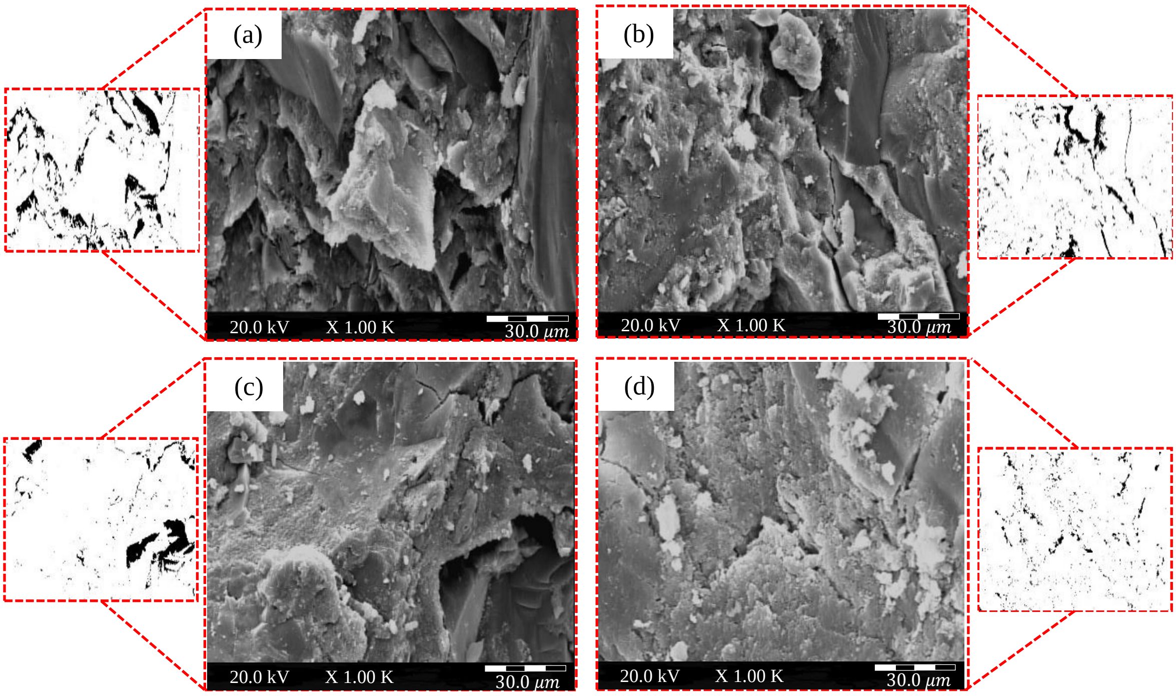

Fig.3. SEM image of surface microstructure of cement mortar for W/B of 0.50: (a) 0%Ms+0%Ns, (b) 9%Ms+0%Ns, (c) 0%Ms+4.2%Ns (d) 9Ms+2.8%Ns.

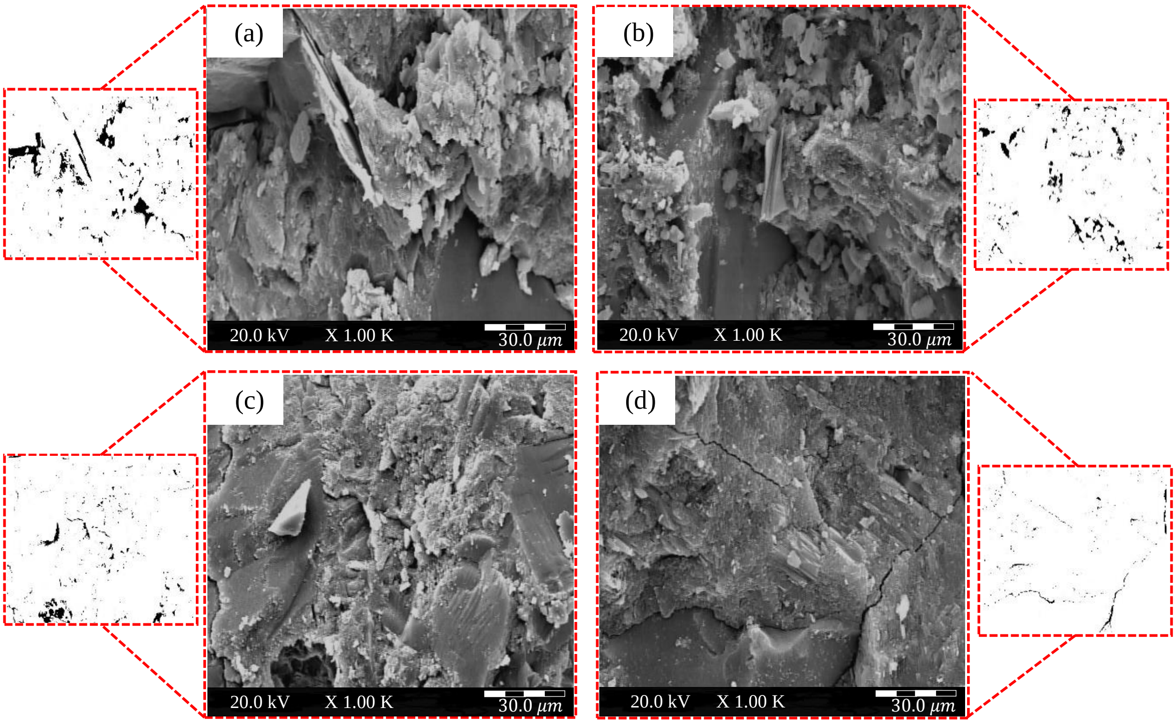

Fig.4. SEM image of surface microstructure of cement mortar for W/B of 0.40: (a) 0%Ms+0%Ns, (b) 9%Ms+0%Ns, (c) 0%Ms+4.2%Ns (d) 9Ms+2.8%Ns.

4. Conclusion

In this research, the synergistic effect of Ns and Ms on porosity and microstructure of the cement mortar were investigated. In this regard, the porosity results have been compared with the microstructure observations. Hence, the following conclusions derived from the experimental porosity results and microstructure observations:

1. Adding nano- and micro-silica gradually decreases the porosity values and also improve the microstructure of the cement mortar.

2. Combined usage of nano- and micro-silica has a synergistic effect which causes the most decrease in porosity values and most improvement in the microstructure of cement mortar compared to using them alone.
3. The lowest value of the porosity and most dense and compact microstructure observed in the NMs-2.8/9 mixture.
4. By reducing the W/B ratio, while the amount of nano- and micro-silica increase the specimens experience a smaller decrease in their porosity.
5. The microstructural observations from FE-SEM images confirm the mentioned reduction trend for porosity values.

REFERENCES

[1] J. Xie, C. Fang, Z. Lu, Z. Li, L. Li, Effects of the addition of silica fume and rubber particles on the compressive behaviour of recycled aggregate concrete with steel fibres, J. Clean. Prod. (2018). doi:10.1016/j.jclepro.2018.06.237.
[2] L.G. Li, Z.H. Huang, J. Zhu, A.K.H. Kwan, H.Y. Chen, Synergistic effects of micro-silica and nano-silica on strength and microstructure of mortar, Constr. Build. Mater. 140 (2017) 229–238. doi:10.1016/j.conbuildmat.2017.02.115.
[3] S.A. Emamian, H. Eskandari-Naddaf, Effect of porosity on predicting compressive and flexural strength of cement mortar containing micro and nano-silica by ANN and GEP, Constr. Build. Mater. 218 (2019) 8–27.
[4] Y. Reches, Nanoparticles as concrete additives: Review and perspectives, Constr. Build. Mater. 175 (2018) 483–495. doi:10.1016/j.conbuildmat.2018.04.214.
[5] Z. Zhang, B. Zhang, P. Yan, Comparative study of effect of raw and densified silica fume in the paste, mortar and concrete, Constr. Build. Mater. 105 (2016) 82–93. doi:10.1016/j.conbuildmat.2015.12.045.
[6] I. Vegas, J.J. Gaitero, J. Urreta, R. García, M. Frías, Aging and durability of ternary cements containing fly ash and activated paper sludge, Constr. Build. Mater. (2014). doi:10.1016/j.conbuildmat.2013.10.070.
[7] A. Mardani-Aghabaglou, G. Inan Sezer, K. Ramyar, Comparison of fly ash, silica fume and metakaolin from mechanical properties and durability performance of mortar mixtures view point, Constr. Build. Mater. 70 (2014) 17–25. doi:10.1016/j.conbuildmat.2014.07.089.
[8] Y.K. Cho, S.H. Jung, Y.C. Choi, Effects of chemical composition of fly ash on compressive strength of fly ash cement mortar, Constr. Build. Mater. 204 (2019) 255–264. doi:10.1016/j.conbuildmat.2019.01.208.
[9] L.G. Li, J.Y. Zheng, J. Zhu, A.K.H. Kwan, Combined usage of micro-silica and nano-silica in concrete: SP demand, cementing efficiencies and synergistic effect, Constr. Build. Mater. 168 (2018) 622–632. doi:10.1016/j.conbuildmat.2018.02.181.
[10] A.K.H. Kwan, H.H.C. Wong, Packing density of cementitious materials: Part 2-packing and flow of OPC + PFA + CSF, Mater. Struct. Constr. (2008). doi:10.1617/s11527-007-9281-6.
[11] R.J. Detwiler, P.K. Mehta, Chemical and physical effects of silica fume on the mechanical behavior of concrete, ACI Mater. J. (1989). doi:10.14359/2281.
[12] D. Perraton, P.C. Aiticin, D. Vezina, Permeabilities of silica fume concrete, Spec. Publ. 108 (1988) 63–84.
[13] V. Antonovič, I. Pundiene, R. Stonys, J. Česniene, J. Keriene, A review of the possible applications of nanotechnology in refractory concrete, J. Civ. Eng. Manag. (2010). doi:10.3846/jcem.2010.66.
[14] X. Liu, L. Chen, A. Liu, X. Wang, Effect of nano-CaCO3 on properties of cement paste, in: Energy Procedia, 2012. doi:10.1016/j.egypro.2012.01.158.
[15] H. Li, H. gang Xiao, J. ping Ou, A study on mechanical and pressure-sensitive properties of cement mortar with nanophase materials, Cem. Concr. Res. (2004). doi:10.1016/j.cemconres.2003.08.025.
[16] A.M. Rashad, A synopsis about the effect of nano-Al2O3, nano-Fe2O3, nano-Fe3O4 and nano-clay on some properties of cementitious materials - A short guide for Civil Engineer, Mater. Des. (2013). doi:10.1016/j.matdes.2013.05.035.
[17] A.M. Rashad, A synopsis about the effect of nano-titanium dioxide on some properties of cementitious materials - A short guide for civil engineer, Rev. Adv. Mater. Sci. (2015).
[18] M. Jalal, E. Mansouri, M. Sharifipour, A.R. Pouladkhan, Mechanical, rheological, durability and microstructural properties of high performance self-compacting concrete containing SiO 2 micro and nanoparticles, Mater. Des. (2012). doi:10.1016/j.matdes.2011.08.037.
[19] L.G. Li, J. Zhu, Z.H. Huang, A.K.H. Kwan, L.J. Li, Combined effects of micro-silica and nano-silica on durability of mortar, Constr. Build. Mater. 157 (2017) 337–347. doi:10.1016/j.conbuildmat.2017.09.105.
[20] G.C. Mostafa Jalal, Ali Reza. Pouladkhan, Hassan Norouzi, Chloride penetration, water absorption and electrical resistivity of high performance concrete containing nano silica and silica fume, Society. (2012). doi:10.1128/JVI.07133-11.
[21] A.M. Sharkawi, M.A. Abd-Elaty, O.H. Khalifa, Synergistic influence of micro-nano silica mixture on durability performance of cementious materials, Constr. Build. Mater. 164 (2018) 579–588. doi:10.1016/j.conbuildmat.2018.01.013.
[22] ASTM, Standard specification for standard sand, C778-13. (2013).
[23] A. Kooshkaki, H. Eskandari-Naddaf, Effect of porosity on predicting compressive and flexural strength of cement

mortar containing micro and nano-silica by multi-objective ANN modeling, Constr. Build. Mater. 212 (2019) 176–191. doi:10.1016/j.conbuildmat.2019.03.243.