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Study on Mechanical Properties of Metakaolin-Based Concretes and Corrosion of Carbon Steel Reinforcement in 3.5% NaCl

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One of the techniques to improve the concrete durability is to use cement materials blended with silica fume, slag and fly ash. The use of calcined clay cement in the metakaolin form as a pozzolan for mortar and concrete has received remarkable interest in recent years. Here, in this study, corrosion behavior and mechanical property of carbon steel rebar in metakaolin cement-based concretes were investigated. To evaluate the effect of high-reactivity metakaolin in the corrosion resistance of the ordinary Portland cement (OPC) concrete, 5 wt%, 10 wt%, 15 wt% and 20 wt% metakaolin replacement levels were done in concrete production. Corrosion rate, electrochemical mass loss, compressive strength, tensile strengths, open circuit potential, and electrochemical impedance spectroscopy (EIS) of the samples were studied and discussed. The electrochemical mass loss of concrete samples revealed that 15 wt% metakaolin sample had smaller mass losses which exhibited an improvement in anticorrosive properties that had led to better corrosion behavior of the carbon steel rebar. The mechanical results of concrete samples indicated a gradually increase in compressive and tensile strengths with the increase in the cement blended with metakaolin. Furthermore, the EIS findings showed that 15 wt% metakaolin sample indicated a higher value of passive film resistance compared to other samples, indicating that more enhancement of corrosion resistance on the surface of the carbon steel rebar. Scanning electron microscopy images revealed that the concrete structure containing 15 wt% metakaolin was denser and more uniform than that of the OPC sample which was in accordance with studies reported by other researchers.

Keywords: Reinforced concrete; Metakaolin; Electrochemical impedance spectroscopy; Corrosion resistance; Mechanical properties

1. INTRODUCTION

The use of mineral additives such as silica fume and fly ash has been confirmed to be an effective method in improving concrete properties [1, 2]. Recently, with increasing environmental concern, using metakaolin as a modifier and optional additive has also shown an increase in interests [3]. Metakaolin is a pozzolanic product that can offer many specific properties [4, 5]. It is available in different types and quality. The purity defines the free lime or binding capacity. Furthermore, metakaolin is an appreciated admixture for cement and or concrete applications [6]. Metakaolin is gradually being used to provide materials with lower porosity, denser microstructure, higher resistance to ions, higher strength, and improved durability [7].

Khatib et al. [8, 9] exhibited that the 20% cement replacement using metakaolin had caused in a considerable 50% enhancement of the compressive strength for mortar. However, by replacing more than 30% of cement by metakaolin, the compressive strength begins to decrease. Justice et al. [10] compared the effects of using two different types of metakaolin on concrete setting time and workability. It was found that metakaolin leads to a substantial reduction in the setting time and reduced the workability of concrete.

Obviously, in high quality and well-designed concrete, the corrosion risk is predictable to be insignificant since it provides physical and chemical protection to the steel rebar [11, 12]. The corrosion of reinforced concrete is commonly studied as an electrochemical procedure [13-15]. Thus, the use of electrochemical methods for the assessment of corrosion behavior of steel rebar in concrete, becomes an outstanding field of durability study [16, 17]. However, much research still needs to be done on the corrosion resistance of the metakaolin-modified concrete. Batis et al. [18, 19] considered the effect of metakaolin content on corrosion resistance of concrete. The Greek kaolin used was thermally studied to the appropriate fineness.

Very few researchers have studied the electrochemical and mechanical properties in metakaolin cement-based concretes. In the present study, mechanical properties and corrosion behavior of carbon steel using metakaolin (0–20%) as partial replacement in ordinary Portland cement (OPC) 3.5% wt% NaCl solution were investigated.

2. MATERIALS AND METHOD

Concrete samples with 10×10×10 cm size were prepared with 0 wt%, 5 wt%, 10 wt%, 15 wt% and 20 wt% replacement of ordinary Portland cement (OPC) by metakaolin. The metakaolin was used as a commercially available natural pozzolan. The chemical compositions and physical properties of the OPC and metakaolin used are indicated in Table 1. The concrete mixture ratios are shown in Table 2 where water to cement ratio of 0.38 was utilized with a poly-carboxilate as superplasticizer to attain desired workability. The mixed cements were prepared by a high-speed mixer to obtain a high level of homogeneous dispersion. Carbon steel rebar with diameter of 12 mm and long of 5 cm was embedded in the cube at a cover of 2 cm. Initially the carbon steel rods ultrasonically washed in acetone solution and rinsed in deionized water. In order to measure gravimetric weight loss, the initial weights of the rebar were obtained using Metler prior to testing.

Table 1. Physical and chemical properties of the ordinary Portland cement and metakaolin

Parameters	OPC	Metakaolin
SiO_2 (%)	20.65	51.74
Al_2O_3 (%)	4.74	42.95
Fe_2O_3 (%)	3.02	0.98
CaO (%)	64.25	0.22
MgO (%)	2.04	0.19
K_2O (%)	0.65	0.13
Na_2O (%)	0.27	0.01
SO_3 (%)	2.96	0.00
LOI (%)	0.88	0.56
Blaine fineness (m^2/kg)	370	2200
Specific gravity (kg/m^3)	3120	2600

Table 2. Details of the concrete mixes

Item	OPC	5 wt%	10 wt%	15 wt%	20 wt%
OPC (kg/m^3)	420	399	378	357	336
Metakaolin (kg/m^3)	0	21	42	63	84
Coarse aggregate (25 mm max) (kg/m^3)	737	737	737	737	737
Fine aggregate (3.8 fineness modulus) (kg/m^3)	996	996	996	996	996
Filler (sand powder) (kg/m^3)	111	111	111	111	111
Water (kg/m^3)	159	159	159	159	159
W/C	0.38	0.38	0.38	0.38	0.38
Super plasticizer (sulphonated naphthalene) (kg/m^3)	3.2	3.2	4.0	4.8	4.8

The corrosion rate of carbon steel rebar was measured by determining the mass loss of rebars [20].

$$Corrosion\ rate = \frac{87.6 \times W}{D \times A \times T} \tag{1}$$

where, *W* and *D* are the weight loss (g) and density of the used material, respectively. *A* and *T* are area of the sample (cm^2) and the time duration (h), respectively.

The open circuit potential (OCP) for the various systems were periodically done using a high-impedance voltmeter with an input resistance of 10 MΩ. A three-electrode system, including of the steel rebar as a working electrode, graphite as a counter electrode and saturated calomel electrode as a reference electrode was used. Two-week analysis were recorded for potential up to 12 weeks of exposure period in the corrosive environment, which was 3.5% w/w NaCl solution. EIS (CorrTest

Instruments Corp., Ltd., China) tests were conducted at OCP with a scanning range of 10 mHz to 100 kHz at the amplitude of 10 mV.

Compressive strength values were obtained in accordance to BS-1881 technique on 10×10×10 cm cube samples with three replicates for all concrete mixtures on 1, 2, 4, 8 and 16 weeks of curing. The morphologies of the samples were examined using scanning electron microscope (SEM, Zeiss Sigma 300 VP).

3. RESULTS AND DISCUSSION

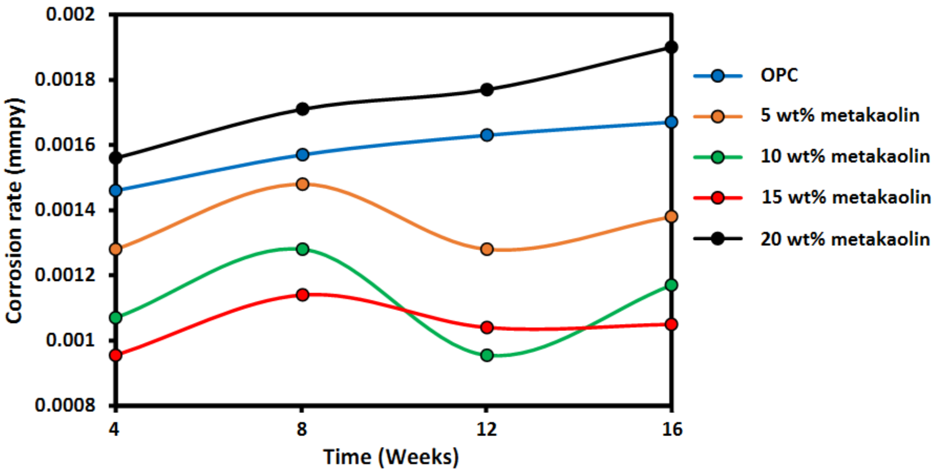

Figure 1. Corrosion rate of carbon steel in concrete exposed to 3.5% NaCl solution

The corrosion rate of reinforced concrete systems is revealed in figure 1. When the metakaolin content increased up to 15 wt%, the corrosion rate gradually reduced. As shown in figure 1, 20 wt% metakaolin exhibits a higher corrosion rate in comparison with other samples. Furthermore, by increasing the exposure time, first the corrosion rate increases and then decreases till 12 weeks exposure time. Finally, the corrosion rate slightly increases for 5-15 wt% metakaolin. But 20% MK addition indicates an increase in corrosion rate from early to final. These observations are due to the process of pore refinement in concrete, which can explain the decrease in weight loss [21]. As a result, the amount of metakaolin reactions are still considerable after a prolonged curing. These findings indicate that 15 wt% of metakaolin provides the best efficiency among other samples for corrosion behavior of steel reinforced concrete.

Measurement of total mass loss during the exposure period provides a relatively accurate prediction for a construction lifetime. Figure 2a shows the mass loss measurements for the tested specimens, so that by increasing the exposure time, losing mass increases. 15 wt% metakaolin sample exhibited an improvement in anticorrosive properties that led to a better corrosion behavior of the carbon steel rebar, whereas other samples revealed greater mass losses. These findings are consistent with the above corrosion measurements. In order to validate the results, the electrochemical mass loss measurements were done from the corrosion current by the Faraday law [22]. Figure 2b shows the electrochemical mass loss of concrete samples in 3.5 wt% NaCl solution. As shown, these results are completely consistent with the mass loss results.

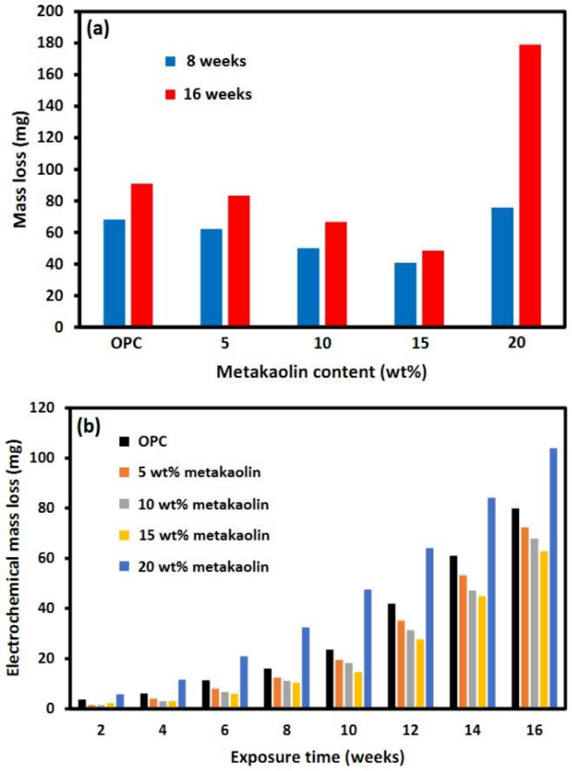

Figure 2. (a) Mass loss and (b) Electrochemical mass loss of reinforced concrete with different metakaolin content at various exposure time in 3.5 wt% NaCl solution

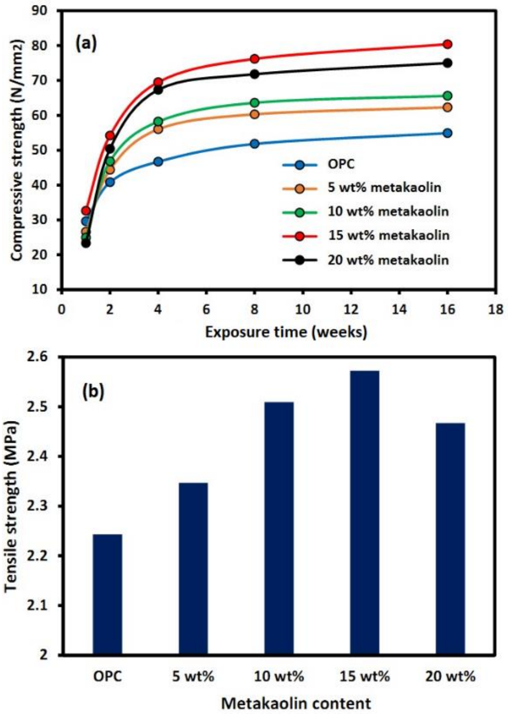

Figure 3. (a) Compressive strength and (b) Tensile strengths of concretes with different metakaolin content

Figure 3a indicates the compressive strength of concretes with different metakaolin content. It is commonly observed that the addition of metakaolin increased the strength of concrete compared to OPC ones. Furthermore, with the exception of 15 wt% metakaolin sample, the metakaolin concretes reveal lower strength after one week in comparison with OPC one, but the samples have a comparable effect on the compressive strength after one week and specifically at 4 and 12 weeks. As shown in figure 3a, concrete with 15 wt% metakaolin shows the best results in all samples. The enhanced strength can be associated to the higher concentration of calcium silicate hydrate ($3CaO \cdot 2SiO_2 \cdot 3H_2O$) in the metakaolin samples, because of the pozzolanic reaction, between the Ca(OH)2 and metakaolin released during the cement hydration, which had caused the occurrence of additional calcium silicate hydrate gel [23].

The splitting tensile strengths (STS) of concrete with metakaolin hydrated for 4 weeks are shown in figure 3b. These results reveal that the STS of the samples increase with the increase of the amount of metakaolin to 15 wt%. The STS of the samples containing 15 wt% metakaolin are higher than the OPC sample by about 13.06%. This improvement can be attributed to the filler effect of metakaolin particles in the interfacial transition zone between cement paste and aggregate in concrete, which had led to an enhancement in the density and improvement in its strength. The reduction of STS in the sample by 20 wt% of metakaolin compared to 15 wt% can be attributed to the dilution effect, which reduced the major phases of βC2S and C3S in the mixed concrete [24]. The dilution effect was due to the replacement of part of the cement with the equivalent amount of methacholine. At higher concentration, the metakaolin particles gather around cement particles and stopped the hydration process which had led to the reduction of hydration production quantities. This can decrease the contact points that act as centers of binding between cement particles [25]. Thus, given that the efficiency of concrete reduced in over 15 wt% metakaolin, as a result it can be considered the economic efficiency as an optimized weight ratio for metakaolin in concrete. These observations are consistent with the work of other researchers [26-28].

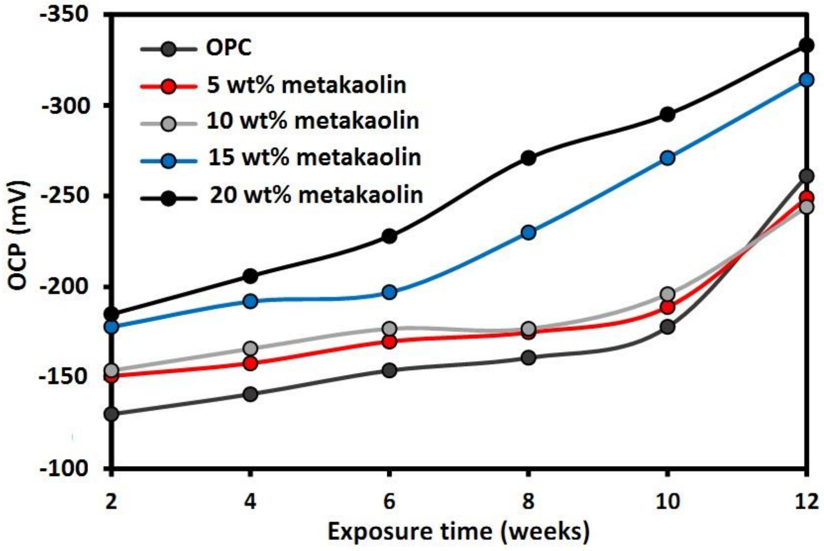

Figure 4. Open circuit potential of carbon steel rebar in concrete with different metakaolin content.

Figure 4 indicates the potential vs. time for carbon steel rebar in concrete with different metakaolin content. There was an open circuit potential (OCP) shifting towards negative direction for 15 wt% and 20 wt% metakaolin addition. The threshold potential of -275 mV was obtained at the exposure period of about 10 weeks and 8 weeks for 15 wt% and 20 wt% metakaolin, respectively. For 5 wt% and 10 wt% metakaolin samples, the threshold potential didn't appear during exposure time which can be attributed to the passive status of the bars during the exposure period. The 5 wt% and 10 wt% metakaolin samples exhibited lower potential values in comparison with OPC concrete. This indicates the influence of metakaolin on the microstructural and diffusion properties of reinforced concrete. Furthermore, significant reduction of the potential can be attributed to the distribution of pore size for the concrete [29].

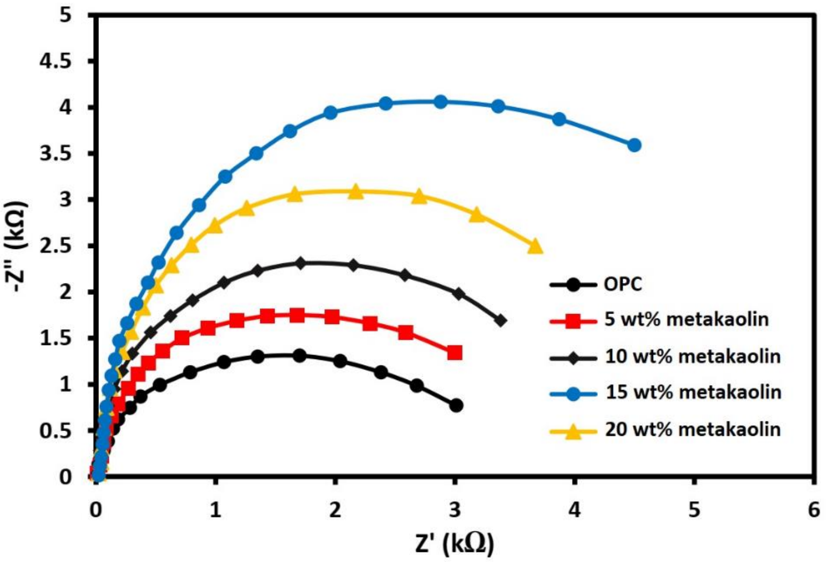

Figure 5. Nyquist plots of steel rebars in concrete with different metakaolin content exposed to 3.5 wt% NaCl solution after 8 weeks exposure time.

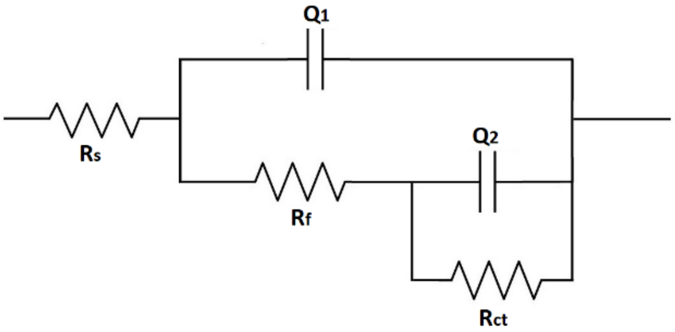

Figure 6. An equivalent circuit used for the fitting of the impedance spectra

EIS technique has been extensively employed in the analysis of the passive layer of rebars due to its capability to characterize redox reactions of steel rebars in an alkaline environment [30]. EIS was conducted to analyze the metakaolin effect on the corrosion behavior of rebars with passive layers in 3.5% NaCl solution. As shown in figure 5, increasing the amount of metakaolin leads to an increase in the capacitive loop radius, which indicates an increase in the corrosion resistance of the reinforced concrete. It can be attributed to the formation of protective passive layer [31]. Figure 6 indicates an equivalent circuit used to model the impedance spectra. Rs is the solution resistance. R_f and R_{ct} are the resistance of passive film and the charge-transfer resistance, respectively [32]. Q_1 and Q_2 are the passive film/solution interface capacitance and double-layer capacitance.

Table 3. Electrochemical parameters from the fitting using the equivalent circuit in Figure 6 for different content of metakaolin exposed to 3.5 wt% NaCl solution after 8 weeks exposure time

Samples	R_s (Ω cm^2)	R_f (kΩ cm^2)	Q_1 (μF cm^{-2})	R_{ct} (kΩ cm^2)	Q_2 (μF cm^{-2})
OPC	16.3	2.21	8.7	3.45	9.7
5 wt% metakaolin	24.5	2.78	4.9	3.86	6.4
10 wt% metakaolin	37.7	3.14	2.2	4.35	3.3
15 wt% metakaolin	22.4	4.98	9.6	6.36	10.8
20 wt% metakaolin	35.4	3.61	2.8	4.95	4.5

As shown in table 2, the value of Q_2 decreases as metakaolin content increases, which reveals that the passive film thickness increased and the resulting protective capacity was enhanced when the metakaolin content of the reinforced concrete was gradually increased.

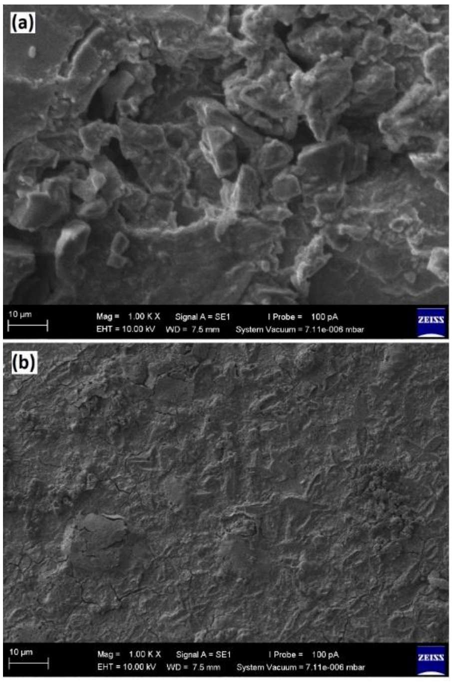

Figure 7. SEM images of concrete samples. (a) OPC concrete, (b) 15 wt% metakaolin concrete exposed to 3.5 wt% NaCl solution after 4 weeks exposure time

The R_f passive film resistance increases as the metakaolin content in alloy is increased, which indicates that the protective feature of the passive film developed is strong [33]. Comparing Q_1 and Q_2, it is found that Q_1 is lower than Q_2 which confirm the formation of passive thin film and the double layer has a high capacitive behavior at the interfaces. In addition, the 15 wt% metakaolin sample showed more resistance to the passive film than the other samples, indicating a further increase in the corrosion resistance of the carbon steel rebar surface.

Figure 7 shows the microstructures of the samples with and without metakaolin after 4 weeks. As shown in Figure 5, the separation and irregularity structures were enhanced with the addition of metakaolin. Figure 5b reveals that the concrete structure containing 15 wt% metakaolin is denser and more uniform than that of the OPC sample which are almost in accordance with studies reported by other researchers [26, 34-36].

4. CONCLUSIONS

In this research, corrosion behavior and mechanical property of carbon steel rebar in metakaolin cement-based concretes were investigated. To evaluate the effect of high-reactivity metakaolin in the corrosion resistance of the OPC concrete, 5 wt%, 10 wt%, 15 wt% and 20 wt% metakaolin replacement levels were done in concrete production. The electrochemical mass loss of concrete samples revealed that 15 wt% metakaolin sample had smaller mass losses which exhibited an improvement in anticorrosive properties that had led to better corrosion behavior of the carbon steel rebar. The tensile and compressive strengths indicated that replacement of metakaolin content up to 15 wt% in OPC improved the mechanical properties of samples. Furthermore, corrosion of carbon steel rebar improved by the metakaolin blended up to 15 wt% in concrete. SEM images revealed that the concrete structure containing 15 wt% metakaolin is denser and more uniform than that of the OPC sample. Furthermore, the EIS findings showed that 15 wt% metakaolin sample had indicated a higher value of passive film resistance compared to other samples, indicating more enhancement of corrosion resistance on the surface of carbon steel rebar.

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References

1. A.A. Ramezanianpour and M.A. Moeini, *Construction and Building Materials*, 163 (2018) 611.
2. P. Shao, L. Ding, J. Luo, Y. Luo, D. You, Q. Zhang and X. Luo, *ACS applied materials & interfaces*, 11 (2019) 29736.
3. A. Al Menhosh, Y. Wang and Y. Wang, *Journal of Engineering*, 2016 (2016) 1.
4. E. Mohseni, M.A. Yazdi, B.M. Miyandehi, M. Zadshir and M.M. Ranjbar, *Journal of Materials in Civil Engineering*, 29 (2017) 04017025.
5. L. Yang, G. Yi, Y. Hou, H. Cheng, X. Luo, S.G. Pavlostathis, S. Luo and A. Wang, *Biosensors and Bioelectronics*, 141 (2019) 111444.

6. A. Menon, C.M. Childs, B. Poczós, N.R. Washburn and K.E. Kurtis, *Advanced Theory and Simulations*, 2 (2019) 1801.
7. Z. Guo, Q. Feng, W. Wang, Y. Huang, J. Deng and Z. Xu, *Procedia Environmental Sciences*, 31 (2016) 644.
8. J. Khatib, E. Negim and E. Gjonbalaj, *World journal of chemistry*, 7 (2012) 7.
9. P. Shao, X. Duan, J. Xu, J. Tian, W. Shi, S. Gao, M. Xu, F. Cui and S. Wang, *Journal of hazardous materials*, 322 (2017) 532.
10. J. Justice and K. Kurtis, *Journal of materials in civil engineering*, 19 (2007) 762.
11. V. Volpi-León, L. López-Léon, J. Hernández-Ávila, M. Baltazar-Zamora, F. Olguín-Coca and A. López-León, *International Journal of Electrochemical Science*, 12 (2017) 22.
12. C. Li, S. Hu, L. Yang, J. Fan, Z. Yao, Y. Zhang, G. Shao and J. Hu, *Chemistry–An Asian Journal*, 10 (2015) 2733.
13. J. Chen and X. Zhang, *International Journal of Electrochemical Science*, 12 (2017) 5036.
14. G. Cao, L. Wang, Z. Fu, J. Hu, S. Guan, C. Zhang, L. Wang and S. Zhu, *Applied Surface Science*, 308 (2014) 38.
15. S. Kakooei, H.M. Akil, A. Dolati and J. Rouhi, *Construction and Building Materials*, 35 (2012) 564.
16. Y.-y. Lu, J.-y. Hu, S. Li and W.-s. Tang, *Electrochimica Acta*, 278 (2018) 124.
17. N. Naderi, M. Hashim and J. Rouhi, *International Journal of Electrochemical Science*, 7 (2012) 8481.
18. G. Batis, P. Pantazopoulou, S. Tsivilis and E. Badogiannis, *Cement and Concrete Composites*, 27 (2005) 125.
19. J. Hu, C. Zhang, B. Cui, K. Bai, S. Guan, L. Wang and S. Zhu, *Applied Surface Science*, 257 (2011) 8772.
20. B. Pradhan and B. Bhattacharjee, *Construction and building materials*, 23 (2009) 2346.
21. K. Bai, Y. Zhang, Z. Fu, C. Zhang, X. Cui, E. Meng, S. Guan and J. Hu, *Materials Letters*, 73 (2012) 59.
22. Y. Zhang, K. Bai, Z. Fu, C. Zhang, H. Zhou, L. Wang, S. Zhu, S. Guan, D. Li and J. Hu, *Applied Surface Science*, 258 (2012) 2939.
23. J. Hu, C. Zhang, S. Guan, L. Wang, S. Zhu, S. Chen, J. Gao, E. Meng, S. Hou and B. Cui, *Materials Letters*, 64 (2010) 2569.
24. J. Hu, G. Shaokang, C. Zhang, C. Ren, C. Wen, Z. Zeng and L. Peng, *Surface and Coatings Technology*, 203 (2009) 2017.
25. J. Rouhi, S. Mahmud, S.D. Hutagalung and S. Kakooei, *Journal of Micro/Nanolithography, MEMS, and MOEMS*, 10 (2011) 043002.
26. A. Ramezanianpour and H.B. Jovein, *Construction and Building Materials*, 30 (2012) 470.
27. H.-S. Kim, S.-H. Lee and H.-Y. Moon, *Construction and building materials*, 21 (2007) 1229.
28. R. Siddique and J. Klaus, *Applied Clay Science*, 43 (2009) 392.
29. F. Husairi, J. Rouhi, K. Eswar, A. Zainurul, M. Rusop and S. Abdullah, *Applied Physics A*, 116 (2014) 2119.
30. Q. Liu, B. Chen and Y. Li, *International Journal of Electrochemical Science*, 11 (2016) 10238.
31. F. Husairi, J. Rouhi, K. Eswar, C.R. Ooi, M. Rusop and S. Abdullah, *Sensors and Actuators A: Physical*, 236 (2015) 11.
32. M. Criado and J.L. Provis, *Frontiers in Materials*, 5 (2018)
33. D. Kong, C. Dong, A. Xu, C. He and X. Li, *Corrosion Engineering, Science and Technology*, 52 (2017) 188.
34. J.H. Zhang, K. Yuan, Z.H. Shui and Y.Y. Wang. *Effect on Structure and Properties of Cement-Based Materials by Polymer-Modified Metakaolin Slurry*. in *Materials Science Forum*. 2018: Trans Tech Publ.

35. M.M. Norhasri, M. Hamidah, A.M. Fadzil and O. Megawati, *Construction and Building Materials*, 127 (2016) 167.
36. E. Kuzielová, M. Žemlička, E. Bartoničková and M.T. Palou, *Construction and Building Materials*, 135 (2017) 306.