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Short Communication

Reinforced Concrete Structure Composition Analysis after Electrochemical Chloride Extraction

Ning Xue[*], *Xingwang Liu, Hanbo Jia, Yingshuai Wu and Jingjun Ma*[*]

College of Science and Technology, Agricultural University of Hebei, Huanghua, 061100, P.R. China
[*]E-mail: mjjwjpmartin@163.com ; xingangliu@yahoo.com

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Corrosion of reinforcing steel bar is one of the major reasons for the deterioration of reinforced concrete structures. Chloride permeation from deicing salts, seawater or other environmental causes is the primary reason for the corrosion. Electrochemical Chloride Extraction (ECE) is a simple and low-cost technique whereby chlorides could be removed from contaminated concrete. However, side effect of the ECE process was commonly observed on the ordinary Portland cement. In this study, we used the ordinary Portland cement as a control group and investigated the ECE efficiency and side effect of the blended cement with different composition. Micro vickers hardness tester and mercury intrusion porosimetry were used for characterizing the microstructural properties of the mortar samples. A higher chloride removal efficiency was observed on the ordinary Portland cement made mortar compared with that of the blend cement made mortar. The microhardness difference before and after ECE process of the mortar sample made by blend cement is much higher than that of the mortar sample made by the ordinary Portland cement.

Keywords: Electrochemical chloride extraction; Reinforced concrete; Cement; Microhardness

1. INTRODUCTION

Deterioration of reinforced concrete structure by steel rebar corrosion is one of the major problems in the field of civil engineering [1-3]. Chloride ion intrusion is the major cause lead to such corrosion according to a spate of report [4-6]. For the traditional repair method, the rust of the steel rebar has to be cleaned by physical or chemical ways and then coated with protective material such as epoxy. Finally, the less permeable concrete was chosen for construction. It can be seen that this method has an obvious drawback of very heavy pressing processes [7, 8]. The surface coating of the steel rebar is also lower the cohesion between the rebar and concrete [9, 10]. Therefore, the development of an alternative method for corrosion concrete structure repair is important in the civil engineering field.

Electrochemical Chloride Extraction (ECE) (also known as desalination process or electrochemical chloride removal treatment) is an alternative technique applied for the extract from the chlorides away from the steel [11-18]. Commonly, about 50 % to 90 % of chloride can be extracted from the concrete and consequently form a high level of passivation film on the steel rebar surface when the chlorides have not penetrated too much beyond the first layer of reinforcing steel. A temporary anode was installed and the steel rebar was used as the cathode. The applied current density is varied from 1 A/m^2 to 10 A/m^2. ECE treatment can be applied in various reinforced concrete structures including highway structures, overpass and mechanical parking system [19, 20]. The ECE process commonly takes one to two months. Some study reported the ECE process for bridge decks required a longer extract period due to the isolated steel and prestressing. The anode could be removed after completion and no further monitoring is required. Some reports indicated the side effects were observed after the ECE process. For example, Orellan and co-workers reported an ECE study which showed the new cementitious phases involving high concentrations of Na, Al and K were formed around the steel [21]. The alkali-aggregate could result in a concrete expansion, which subsequently provides a pathway for chloride further intrusion and then cause the crack of the concrete. Page and co-workers demonstrated the crack could form even at low alkali ions concentrations after the ECE process [22-24]. The possible reason of the cracking is due to the presence of alkali silica gel, which leads the partial expansion. Because the hydrogen could penetrate into the steel during the ECE process by the hydrogen production of the cathode, the hydrogen embrittlement is another side effect of the ECE treatment [25]. For hardness analysis, several reports claimed the decreasing of the concrete hardness around the steel rebar after the ECE process [26], while Bertolini and co-authors showed no difference of the hardness before and after ECE process [27]. Most of this work was conducted by the reinforced concrete prepared by the ordinary Portland cement. In this work, we compared the ECE efficiency and side effects of reinforced concrete prepared by the ordinary Portland cement and blended cement. The physical properties of the concrete around the steel rebar were characterized in detail.

2. EXPERIMENTS

2.1 Mortar preparation

Ordinary Portland cement 42.5, pulverised fuel ash and ground blast furnace slag were employed for constructing sample mortars. The mortar samples were constructed in size of 40 × 50 × 100 mm. The steel rebar with diameter of 8 mm with 130 mm in length were embedded in into the concrete. One pure ordinary Portland cement made mortar (denoted as OPC-1) and four blend mortars were prepared for analysis. The composition of four blend mortars were 80% ordinary Portland cement + 20% pulverised fuel ash (denoted as OPC-2), 60% ordinary Portland cement + 40% pulverised fuel ash (denoted as OPC-3), 80% ordinary Portland cement + 20% ground blast furnace slag (denoted as

OPC-4) and 60% ordinary Portland cement + 40% ground blast furnace slag (denoted as OPC-5), respectively. The chloride corrosion was achieved by adding 3 % of NaCl into the mortar during the mixing procedure. After casting and demould, the mortars were placed into a standard curing chamber for 1 month before testing.

2.2 Electrochemical chloride extraction process

The ECE process was carried out in plastic reservoirs with a titanium mesh wrapped external anode. A maximum current density of 6 A/cm^2 and the maximum possible extraction voltage of 32 V were used for ECE process. The mixture of the 0.1 M NaOH and H_3BO_4 was used as the electrolyte. The whole ECE process was carried out for 28 days.

2.4 Chemical content determination

The chemical content determination was performed the end of the ECE treatment. The pore fluid was extracted and then analyzed by atomic absorption spectroscopy. $OH^—$, Na^+ , K^+ , $SO_4^{2—}$ and $Cl^—$ contents were then analyzed. Spectrophotometric methods (Halo RB-10, Dynamica Pty Ltd,) were employed to determine chloride and sulfate concentrations [28]. Concentrations of sodium and potassium ions were determined by flame photometry (Elico-CL378). Hydroxyl ion concentrations were determined by titration with standard nitric acid [29]. The total chloride concentration was analyzed by dissolving the powder in hot nitric acid. Standard nitric acid titration was used for hydroxyl ion concentration determination.

2.5 Microhardness analysis

Micro vickers hardness tester (HM-200 Series Mitutoyo) was used for microhardness analysis. The sample was prepared by the cutting the middle of the mortar at left to the cathode. 9 μm alumina, ethanediol and 1 μm diamond paste were consequently used for sample polishing. Different distances from steel rebar were used for microhardness measurement. Ten readings were conducted and averaged for each sample.

2.6 Pore size distribution analysis

Pore size distribution was measured by the mercury intrusion porosimetry using abound 30mg fragmental pieces. The sample was soaked into propanol for 3 days for removing water. Then, the samples were dried using N_2 gas and placed in a desiccator for mercury intrusion porosimetry analysis. The total intruded volume of mercury represents the porosity of the sample.

3. RESULTS AND DISCUSSION

The hydroxyl ions of the all samples were analysed and the results were presented in the Figure 1. Figure 1 shows the hydroxyl ions profiles of all samples at different distances from the steel rebar. It can be seen that the hydroxyl ions mainly concentrated around to the steel and decreasing along with the distance increasing. Values of 782, 658, 642, 555 and 570 mM were observed for OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 around the steel rebar, respectively. The higher hydroxyl ions concentration result in a higher pH condition. The highest pH value was observed at OPC-1, while the ordinary Portland cement and ground blast furnace slag (OPC-4 and OPC-5) made mortar showed the lowest pH condition. In all cases, the high pH value could result alkali–silica reaction. This reaction could result in the expansion and the formation of calcium silicate hydrate. The cracking in concrete could be caused by the alkali–silica reaction However, according to the Tritthart et al. [14] report, the alkali–silica reaction after ECE process considers as harmless under normal condition.

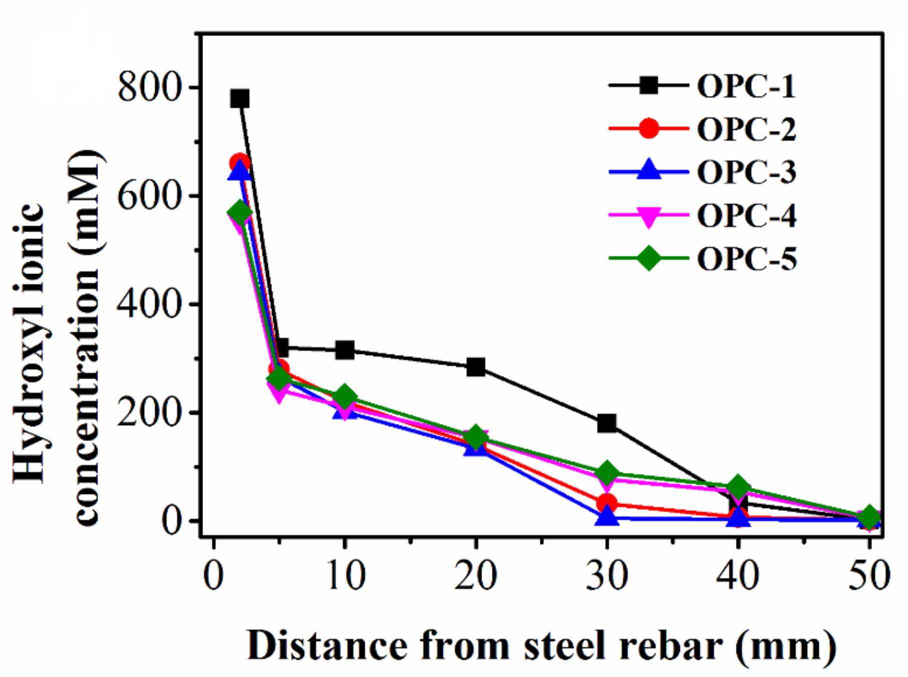

Figure 1. Hydroxyl ionic concentration of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 at different distances from the rebar.

Figure 2A shows the free chloride contents of the mortar samples. It can be seen that the chloride extraction efficiency of OPC-1 showed a higher value compared with that of the cement + pulverised fuel ash made concrete and the cement + slag made concrete. Therefore, the involving of the pulverised fuel ash and slag could result the limitation of the chloride diffusion due to the pore surface interactions, which result in the low ECE performance [30]. Moreover, the slag involved concrete showed a higher chloride extraction efficiency compared with that of the pulverised fuel ash involved concrete. Figure 2B shows the total chloride profiles of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5. A similar result was observed on the total chloride profiles, which prove the above speculation. Moreover, a linear relationship between the free and total chloride was obtained in the cases of ement + pulverised fuel ash made concrete and the cement + slag made concrete, suggesting the blend cement owing a higher chloride binding capacity than that of the pure Portland cement [31]. The presence of enough C_3A (3 CaO • Al_2O_3) is essential for achieving a well overall binding capacity. C_3A is the most important substance for the formation of Friedel's salt during the casting. Previous study showed the presence of the either pulverised fuel ash and slag could lower the C_3A content and affect the binding capacity of the formed concrete, consequently lower the chemical binding ability towards chloride ions [32]. On the other hand, the presence of the either pulverised fuel ash and slag could lead to the formation of calcium–silicate–hydrates. The presence of high concentration of calcium–silicate–hydrates could accelerate the chloride adsorption process [33, 34].

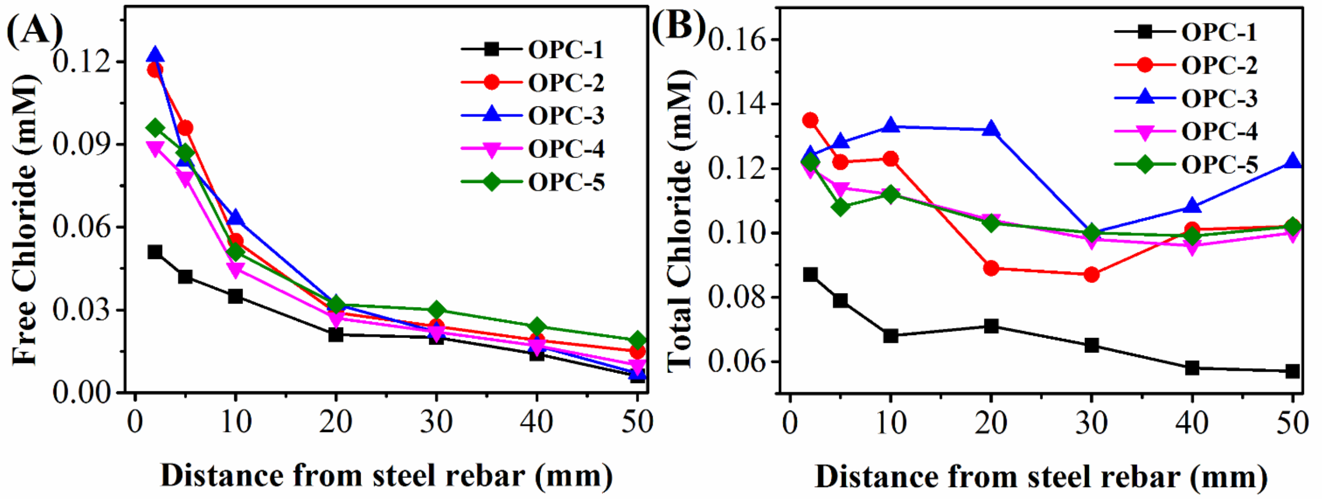

Figure 2. (A) Free chloride content and (B) total chloride content of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 at different distances from the rebar.

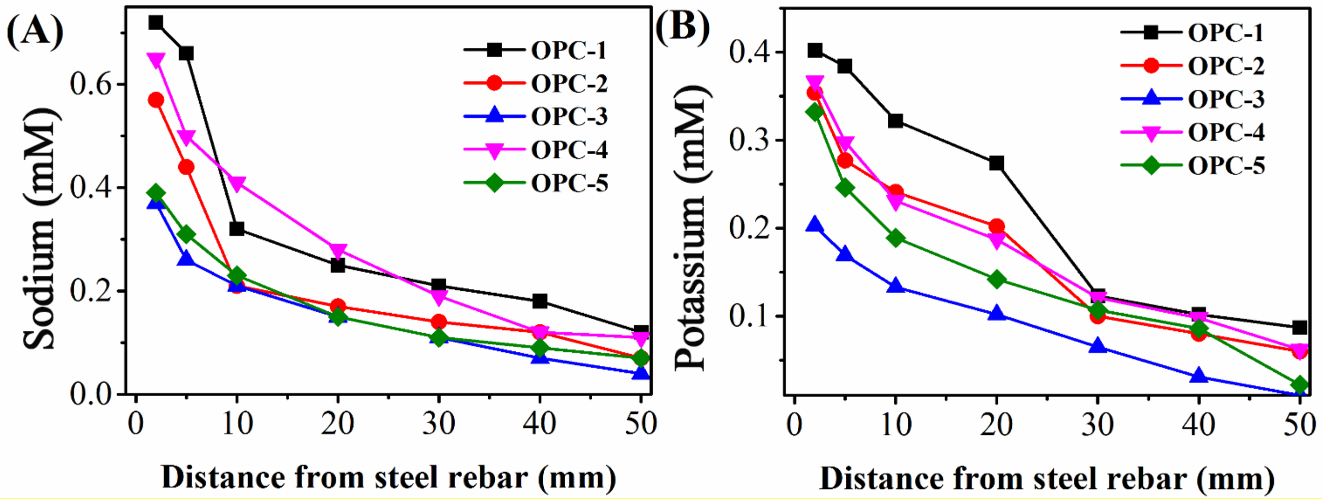

Figure 3. Total (A) sodium and (B) potassium content of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 at different distances from the rebar.

The evidence of the limitation of the ions diffusion in cement + pulverised fuel ash made concrete and the cement + slag made concrete was also confirmed by the sodium and potassium concentrations profiles. Figure 3A and 3B show the total sodium content and total potassium content of all samples after ECE process. As shown in the figure, the migration of the Na^+ and K^+ at cement + pulverised fuel ash made concrete and the cement + slag made concrete were clearly lower than the value in the ordinary Portland cement made concrete. During this ECE process, the cations such as Na^+ and K^+ migrate to the steel rebar, while the Cl^- ions were taken out of the concrete structure [35]. The lower cations concentration further proved the limitation of the ions diffusion in the blend cement made concrete. Moreover, the higher ratio of either pulverised fuel ash and slag could decrease the ions diffusion performance. Therefore, the Na^+ and K^+ concentration of OPC-3 and OPC-5 were lower than that of the OPC-2 and OPC-4, respectively. On the other hand, the sulfate ionic concentration increased after pH value increasing, especially the area near the steel cathode.

Micro vickers hardness tester was used for microhardness analysis. Figure 4A and 4B show the microhardness profiles of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 before and after ECE process at different distances from the rebar, respectively. A lower microhardness was observed on the area of close to the steel rebar compared with other areas in OPC-1, while the blend cement made concrete showed no such trend. Moreover, a significant microhardness decreasing was observed after the ECE treatment, while the microhardness showed no clear change tendency in blend cement made concrete after the ECE process. However, the average microhardness of all samples after the ECE process showed declines compared with their original values. Therefore, overall, the microhardness of the concrete could be affected by the ECE process. The result shows a good agreement with the previous report [36]. In both pulverised fuel ash and slag involved mortar samples, the average microhardness showed a decreasing when the content of the Portland cement decreasing. However, the addition pulverised fuel ash could enhance the greater density and impermeable microstructure [37], while the addition of slag could exhibit inherent protective qualities against chloride attacks [38].

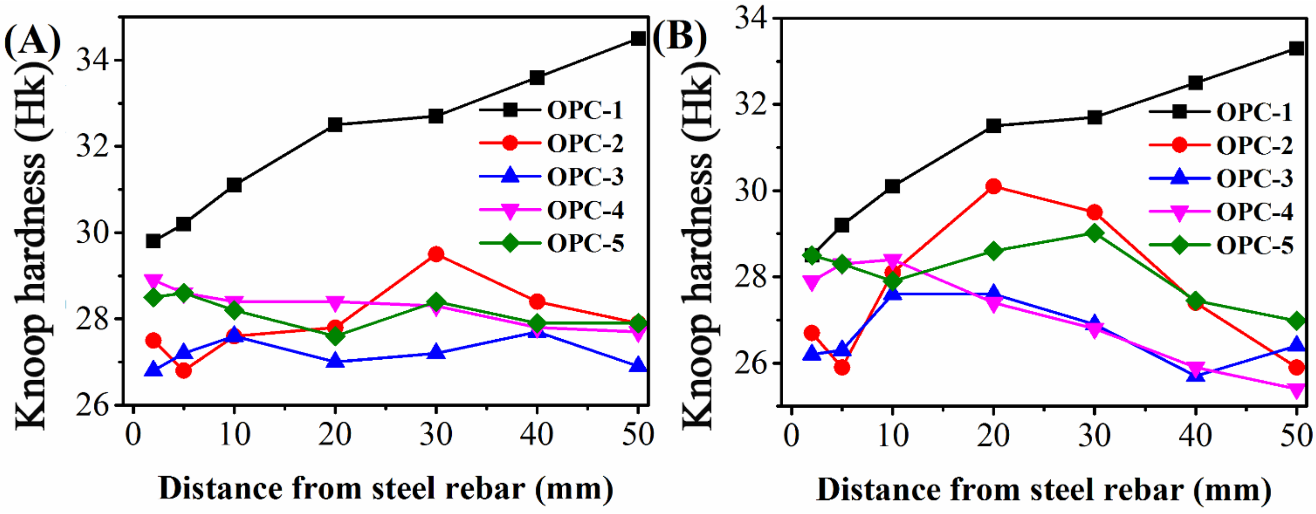

Figure 4. Microhardness profiles of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 (A) before and (B) after ECE process at different distances from the rebar.

The porosity of all samples was determined by the mercury intrusion porosimetry method. Figure 5A and 5B shows the cumulative pore size distribution of the OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 before and after ECE process, respectively. It can be seen that the OPC-1 showed a clear higher porosity after ECE process compared with that of the value obtained before the ECE process. The total porosity of the OPC-1 was obtained to be 0.1255 cm^3/g, which showed a increasing of 16 % porosity compared with the value obtained before the ECE treatment (0.1082 cm^3/g). On the other hand, the blend cement made concrete showed a reverse behaviour. After the ECE treatment, the porosity of both blend cement made concrete exhibited slight declines. Moreover, the lower Portland cement ratio showed less porosity, suggesting both pulverised fuel ash and slag could result a generally tighter microstructure after the ECE treatment.

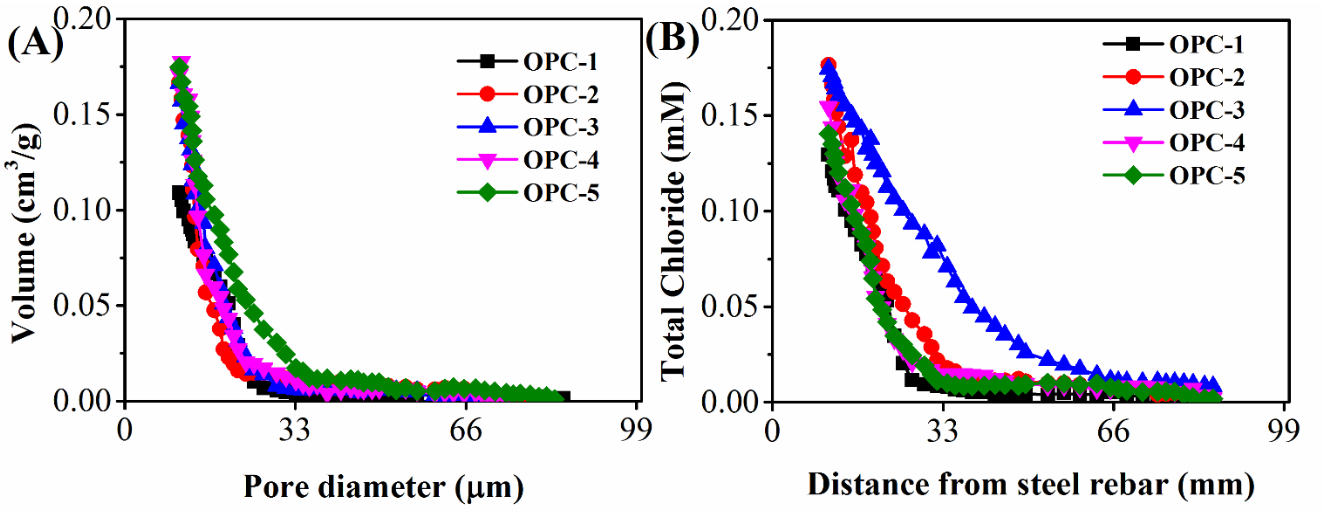

Figure 5. Cumulative pore size distribution of OPC-1, OPC-2, OPC-3, OPC-4 and OPC-5 (A) before and (B) after ECE process.

4. CONCLUSIONS

In conclusion, our carried the ECE process efficiency and side effect comparison study of the concrete made by Portland cement, Portland cement + pulverised fuel ash and Portland cement + ground blast furnace slag. The comparison results suggest that the extraction efficiency of Portland cement made concrete showed a higher value compared with that of the blend cement made concrete. A higher hydroxyl ionic concentration and pH value was obtained at the area near steel rebar. A higher sodium and potassium content was obtained with Portland cement made concrete compared with that of the blend cement made concrete. The microhardness characterization was indicated the addition of pulverised fuel ash and ground blast furnace slag could significant lower the microhardness of the concrete. The pore size distribution characterization suggests that the Portland cement made concrete showed a clear higher porosity after ECE process, while both blend cement made concrete showed decreasing of the porosity.

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References

1. P.K. Mehta and R.W. Burrows, *Concrete International,* 23 (2001) 57
2. G. Al-Sulaimani, M. Kaleemullah and I. Basunbul, *Structural Journal,* 87 (1990) 220
3. J. Rodriguez, L. Ortega and J. Casal, *Construction and building materials,* 11 (1997) 239
4. R. Browner, *Durability of building materials,* 1 (1982) 113
5. M. Ibrahim, A. Al-Gahtani, M. Maslehuddin and A. Almusallam, *Construction and Building Materials,* 11 (1997) 443
6. U. Neubauer and F. Rostasy, Design aspects of concrete structures strengthened with externally bonded CFRP-plates, *Proceeding of the Seventh International Conference on Structure Faults and Repair,* 8 July 1997. Volume 2: Concrete and Composites, 1997.
7. V. Karbhari, J. Chin, D. Hunston, B. Benmokrane, T. Juska, R. Morgan, J. Lesko, U. Sorathia and D. Reynaud, *Journal of composites for construction,* 7 (2003) 238
8. G.J. Al-Sulaimani, A. Sharif, I.A. Basunbul, M.H. Baluch and B.N. Ghaleb, *Structural Journal,* 91 (1994) 458
9. A. Cheng, R. Huang, J. Wu and C. Chen, *Construction and Building Materials,* 19 (2005) 404
10. M. Manna, G. Naidu, N. Rani and N. Bandyopadhyay, *Surface and Coatings Technology,* 202 (2008) 1510
11. J. Mietz, *Institute of Materials, 1 Carlton House Terrace, London, SW 1 Y 5 DB, UK, 1998. 57,* (1998)
12. N.R. Buenfeld, G.K. Glass, A.M. Hassanein and J.-Z. Zhang, *Journal of Materials in Civil Engineering,* 10 (1998) 220
13. J. Broomfield and N. Buenfeld, *Transportation Research Record: Journal of the Transportation Research Board,* (1997) 77
14. J. Tritthart, *Special Publication-Royal Society of Chemistry,* 183 (1996) 433
15. X. Wang, Q. Yu, C. Deng, J. Wei and Z. Wen, *Journal of Wuhan University of Technology-Mater. Sci. Ed.,* 22 (2007) 764
16. J. Carmona, M.-Á. Climent, C. Antón, G. de Vera and P. Garcés, *Materials,* 8 (2015) 2901
17. X. Liu, N. Xue, H. Jia, Y. Wu and J. Ma, *Int. J. Electrochem. Sci,* 11 (2016) 6696
18. J. Huang and A. Wang, *Int. J. Electrochem. Sci,* 11 (2016) 4667
19. C. Andrade, M. Castellote and C. Alonso, An overview of electrochemical realkalisation and chloride extraction, Proceedings of 2nd Int. RILEM/CSIRO/ACRA Conference on Rehabilitation of Structures, Melbourne, Australia, 1998, pp. 1.
20. M. Kliškić, J. Radošević, S. Gudić and V. Katalinić, *Journal of Applied Electrochemistry,* 30 (2000) 823
21. J.C. Orellan, G. Escadeillas and G. Arliguie, *Cement and Concrete Research,* 34 (2004) 227
22. C. Page and S. Yu, *Magazine of concrete research,* 47 (1995) 23
23. Y. Zheng, Z. Wang, F. Peng, A. Wang, X. Cai and L. Fu, *Fullerenes, Nanotubes and Carbon Nanostructures,* 24 (2016) 149
24. A. Wang, H.P. Ng, Y. Xu, Y. Li, Y. Zheng, J. Yu, F. Han, F. Peng and L. Fu, *Journal of Nanomaterials,* 2014 (2014) Article ID 451232
25. M. Siegwart, J. Lyness, B. McFarland and G. Doyle, *Construction and Building Materials,* 19 (2005) 585
26. G. Sergi and C. Page, *TRL Contractor Report,* (1992)

27. L. Bertolini, S. Yu and C. Page, *Advances in Cement Research*, 8 (1996) 93
28. G. Jeffery, J. Bassett, J. Mendham and R. Denney, *John Wiley and Sons Inc., New York NY*, 10158 (1989)
29. M. Yoshio, H. Waki and N. Ishibashi, *Journal of Inorganic and Nuclear Chemistry*, 32 (1970) 1365
30. C. Page, N. Short and A. El Tarras, *Cement and concrete research*, 11 (1981) 395
31. W. Holden, C. Page and N. Short, *Corrosion of reinforcement in concrete construction*, (1983) 143
32. H. Hilsdorf and J. Kropp, Performance criteria for concrete durability, CRC Press2004.
33. M. Maslehuddin, C. Paget and Rasheeduzzafar, *Magazine of Concrete Research*, 49 (1997) 5
34. J.O. Herrera, G. Escadeillas and G. Arliguie, *Cement and concrete research*, 36 (2006) 1939
35. H. Wei, P. Zhang, Y. Cui, X. Zhao and C. Sun, *Yingyong Jichu yu Gongcheng Kexue Xuebao/Journal of Basic Science and Engineering*, 22 (2014) 556
36. J. Miller, Structural aspects of high powered electrochemical treatment of reinforced concrete, Proceedings of the International Conference on Corrosion and Protection of Steel in Concrete, 1994, pp. 24.
37. S.E. Hussain, *Materials Journal*, 91 (1994) 264
38. M.G. Ali, *Materials Journal*, 90 (1993) 247