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Electrochemical chloride extraction (ECE) based on the high performance conductive cement-based composite anode

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HIGHLIGHTS

- The ECE efficiency for CCM anode was as high as that of traditional stainless anode.
- The content of carbon fiber affects the ductility and conductivity of CCM anode.
- The CCM anode thickness influences the ECE efficiency.
- The CCM anode has an excellent cracking resistance capacity and could be re-used.

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ABSTRACT

The chloride ions, imbibition in the reinforcement concrete, are detrimental to the durability of the material. In this paper, a low shrinkage and high ductile conductive cement-based mortar was developed as a novel external anode for electrochemical chloride extraction (ECE). The electricity resistivity, fracture energy and drying shrinkage of mortar with different length, volume fraction of carbon fiber were investigated to optimize mix proportion of conductive cement base mortar (CCM). Subsequently, the proposed CCM with good performance was then utilized as the anode to remove the chloride ions electrochemically from three types of reinforced concrete. The chloride ions distribution in concrete and CCM anode were obtained to evaluate the electrochemical chloride extraction (ECE) efficiency. Additionally, the microstructures, elements distribution and calcium hydroxide content of CCM anode and ITZ were achieved for the further mechanism investigation. Experimental results indicated that the ECE efficiency for CCM anode was as high as that of traditional stainless mesh anode. The CCM anode with 0.8% volume fraction of carbon fiber exhibits excellent ductile and conductivity performance. Furthermore, CCM anode thickness influences significantly on the chloride removal efficiency and residual chloride proportion in concrete and CCM anode. And 10 mm thickness of CCM anode was a suitable value to ECE treatment of reinforced concrete. The microstructure and calcium hydroxide content in CCM anode showed no degradation after 35 days of ECE treatment, which indicated that the CCM anode have an excellent cracking resistance capacity and could be re-used.

1. Introduction

Chloride ion migration into the concrete cover and cause the depassivation and corrosion of the steel bar [1,2], resulting in cracking and loss of carrying capacity are mainly durability problem of reinforced concrete serviced in marine environment [3,4]. And the cost of corrosion is 3.34% of Chinese GDP according to 'The Chinese Science' reported in 2016. Over the last ten years, a number of protection technologies have been developed and used to promote the durability of new reinforced concrete [5–7]. These technologies including the use of high performance concrete, epoxy coated reinforcements, silane coating and cathodic protection, and have been used in Hangzhou Bay Bridge, Hongkong-Zhuhai-Macao cross-sea passages and Jiaozhou bay subsea tunnel [8,9]. However, lots of reinforced concrete structures built in the second half of the last century contaminated with seawater or salt fog, and continue to damage at a rapid speed due to corrosive reinforced bar. The traditional repair method replacing corroded concrete with fine aggregate concrete has been used widely [10]. Electrochemical chloride extraction (ECE), which since the early 1970s, offers a non-destructive treatment method of rehabilitation of such structures [11,12]. In the electrochemical chloride extraction process, negatively charged chloride ions are *transferred* in

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the direct-current away from the steel bar toward the positively charged anode, 40–55% of the total chloride can *be removed from* the corroded concrete within a relatively short period. And the formation of a $Ca(OH)_2$ layer and sodium-rich phases on the steel surface due to ECE treatment would also increase the chloride threshold level [13–15]. Therefore, the corrosion risk of steel bar was decreased and the service life of reinforced concrete structure would be prolonged. And various case studies and experiments have been carried out [16], and a state-of-the-art report by Mietz [17] has been published.

When the ECE treated reinforced concrete structure is still working in a marine environment, the external chloride ions will inevitably penetrate into the concrete again, combined with remaining chloride ions, the secondary corrosion of reinforced bar could be happened. In order to solve this problem, the ingress of chloride ions into the ECE treated concrete structure is required to be resisted. Some strategies including surface coating treatment, repeated ECE treatments and cathodic protection, which have the potential to reduce ingress of chloride ion and corrosion of reinforced bar, needed to be developed and applied to ECE treated concrete structures [18]. The traditional anodic systems including stainless steel and titanium mesh are easily damaged due to anodic reaction present in the ECE treatment. The development of new types of anode for ECE with surface protection, possibility of reutilization properties and adaptation to various types of surfaces is very interesting. Conductive cement-based composites (CCC) and carbon fiber reinforced polymer (CFRP) has become a potential candidate as a new type of anode. Experimental results from Zhu [19,20] shown that the CFRP could be used as anode with excellent performance in the ECE treatment system, and this new anode was not significantly damaged after ECE treatment and anodic polarization.

The conductive behaviour of cement-based composites could be obtained by the addition of conductive materials including graphene, carbon fibers or carbon nanotube [21–23]. And experimental results from Hou [24] and Bertolin [25] have indicated the CCM could be used as anodes for cathodic protection in concrete structure. More than 40,000 m^2 of reinforced concrete has been cathodic protected by using conductive cement-based mortar in 2006. And J. Carmona [26] also developed a new anodic system made up with a graphite–cement paste 50–50% in mass with low thickness, which has shown comparable performances to other anodes could be widely used to ECC. The cement-based composite anode could also be sprayed on the surface of concrete structure [27]. A new conductive cement paste anode with a mass composition of 1/3 cement (same cement used for the concretes, 1/3 graphite powder and 1/3 water) has also been developed by A. Pérez, and the ECE efficiency of new anode was same as that obtained with a traditional Ti-RuO_2 anode [28].

The overall *goal* of this investigation is to develop a commercial conductive cement-based mortar (CCM) with low cracking risk. And the effectiveness and efficiency of electrochemical chloride extraction from chloride contaminated reinforced concrete by using this new anode with different thickness of the CCM layer were examined. The performance of the ECE was compared with the results using stainless steel mesh anode. And the microstructure of new types of CCM anode and interface zone between concrete and anode after the electrochemical treatment was also carried out.

2. Experimentation

2.1. Reinforced concrete specimen preparation

P.O.42.5 Ordinary Portland cement and P.I.52.5 Portland cement in accordance with Chinese standard GB175-2007 were used to prepare medium strength concrete (No. L35) and high strength concrete (No. L50 and LF50), respectively. S95 GGBS (Chinese standard GB/T18046-2008) and Class I fly ash (as per Chinese standard GB1596-2005) were used to replace cement. The coarse aggregate was crushed granite with particle size of 5–25 mm. And the fine aggregate was river sand with fineness modulus of 2.6. A polycarboxylic super plasticizer was used to keep the slump of fresh concrete in the range of 140 mm to 180 mm. Based on a large number of trials and durability tests, high content of GGBS and Fly ash could improve the workability of fresh concrete, chloride bound capacity and reduce the hydration heat of concrete. Therefore, *it is determined that* the optimized mixture proportion LF50 mixed with 17% fly ash and 32% GGBS and with w/c = 0.35 was identified and had used in lining concrete structure of Jiaozhou subsea tunnel

Table 1
Mix proportions of concretes.

No.	kg m^{-3}					
	Cement	GGBS	Fly ash	Sand	Aggregate	Water
L35	410	0	0	668	1240	182
L50	470	0	0	760	1090	165
LF50	240	150	80	760	1090	165

Table 2
Compressive strength and initial chloride ions content of concretes.

No.	Initial chloride ions content/%concrete	Compressive strength/Mpa		
		3 d	7 d	28 d
L35	0.293	20.71	27.08	44.17
L50	0.283	45.35	54.71	57.52
LF50	0.288	42.55	54.38	63.58

Table 3
Properties of carbon fiber.

Diameter (μm)	Carbon content (w_c%)	Tensile strength (MPa)	Young's modulus (GPa)	Electrical resistivity (Ω·cm)
7 ± 0.2	≥96	4900	240	1.5×10^{-3}