Pergamon

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Cement and Concrete Research 34 (2004) 1781–1785

CEMENT AND CONCRETE RESEARCH

The influence of mineral admixtures on resistance to corrosion of steel bars in green high-performance concrete

Wei Sun*, Yunsheng Zhang, Sifeng Liu, Yanmei Zhang

Department of Materials Science and Engineering, Southeast University, Nanjing 210096, PR China

Received 2 February 2002; accepted 7 January 2004

Abstract

In this paper, the influences of the types, amount and adding approaches of mineral admixtures on pH values, electrical resistance of concrete, anodic polarization potential and mass loss ratio of steel bars in concrete subjected to 50 immersion–drying cycles were investigated. The testing results showed that the addition of mineral admixtures reduced the pH values of the binder pastes in green high-performance concrete (GHPC), especially when two or three types of mineral admixtures were added at the same time (double- or triple-adding approaches), whereas the final pH values were still above the critical breakage pH value of passivation film on the steel bar surface (11.5). Double- and triple-adding approaches also greatly increased the electrical resistance of concrete, which led to a delay in the initial time of corrosion and a decrease in the corrosion rate of steel bars. Additionally, double- and triple-adding mineral admixtures, instead of single-adding, fly ash can reduce the corrosion of steel bars when a large amount of fly-ash replacement was used. All the details of this paper provided a method to reduce or prevent the corrosion of steel bar in concrete, especially for the application in aggressive marine environments.

Keywords: Corrosion of steel bars; Mineral admixtures; High-performance concrete

1. Introduction

Green high-performance concrete (GHPC) is a different type of concrete material, which has been developed in recent years on the basis of high-performance concrete and environment protection technology [1]. One of the main characteristics of GHPC is that using different types of mineral admixtures (fly ash, slag or silica fume) to partially replace Portland cement. When these different reactive mineral admixtures are added into concrete at the same time, they develop their own characteristics with the development of time, so that the physical, mechanical and durability properties of concrete will not be reduced when a large amount of mineral admixtures are added into concrete. For example, in the case of addition of silica fume, slag and fly ash at the same time, silica fume provides main strength amongst these three types of mineral admixtures before 7 days due to its highly early pozzolanic reaction, then, slag begins develop its strong pozzolanic effect. After 28 days, fly ash also gradually exhibits its own properties and provides its contributions to the strength of concrete.

Despite these advantages mentioned above, GHPC also has some disadvantages such as the decrease of the pH values of pore solution in concrete and the change of electrical resistance caused by a large amount of different types mineral admixtures [2–5]. As a result, the corrosion behavior of steel bars in GHPC is quite different from that of normal-strength concrete (NSC). Thus, studies on the influence of types, amount and adding approaches of mineral admixtures on the corrosion of steel bar are very important to further develop and apply GHPC in civil engineering, especially in ocean engineering.

2. Materials and methods

2.1. Materials

Graded 42.5 ordinary Portland Cement supplied by Hua Xin Cement in Hu Bei province, P.R. China, was used, complying with Chinese Standard GB175-92, similar to ASTM C150 type II cement.

* Corresponding author. Tel.: +86-25-379-4619.
E-mail address: sunwei@seu.edu.cn (W. Sun).

0008-8846/$ – see front matter © 2004 Published by Elsevier Ltd.
doi:10.1016/j.cemconres.2004.01.008

Table 1
Compositions and physical properties of raw materials

Materials	Chemical compositions (%)								Specific surface (m^2/kg)	Water demand ratio (%)
	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	SO_3	IL		
Cement	21.47	5.80	4.04	–	59.64	3.24	2.08	2.44	310	–
Fly ash	45.38	33.53	5.29	4.71	3.16	2.81	0.43	5.3	345	95
Slag	34.76	15.39	1.20	–	35.86	9.07	0.81	–	530	99
Silica fume	94.48	0.27	0.87	–	0.54	0.91	–	1.9	20000	–

Graded I fly ash, ground blast furnace slag and silica fume were employed for mineral admixtures to partially replace cement.

A powder-based sulfonate, naphtha-based superplasticizer called FDN-9001, supplied by Huao Yuan Additive Plant, was incorporated. FDN-9001 contains retarding composite. The water-reduction amounted to 25%.

The maximum size of the coarse aggregate was 10 mm, and the fineness modulus of fine aggregate was 2.80.

The chemical compositions and physical properties of materials were listed in Table 1.

2.2. Methods

2.2.1. Immersing–drying cycles test

First, steel bars $\Phi 6 \times 100$ mm should be prepared, then, the surface on these steel bars was treated with HCl. After that, these treated steel bars were embedded in the center of $40 \times 40 \times 160$ mm^3 concrete specimens, prepared according to the mix program (Table 2). These concrete specimens were demoulded after 24 h and conditioned for 28 days at 20 °C, relative humidity 95 or greater. Three specimens were made for each batch, and the experimental results were averaged.

The following was the schedule of immersing–drying cycles:

First, all concrete specimens were immersed in 3.5% NaCl solution for 4 h, then dried at 20 °C for 1 h, after that, these specimens were dried at 60 °C for 19 h. The above procedure was only one cycle. The specimens were broken after 50 immersing–drying cycles, and then, these rusted steel bars were taken out and washed with HCl. The weights of the steel bars were measured, and the mass loss mass of the steel bars was calculated.

2.2.2. Anode polarization test of steel bar

The Φ 6×100 mm steel bars, whose surface was treated in HCl solution, were embed in the middle of the steel mould with the size of $30 \times 30 \times 90$ mm. Fresh concrete, prepared according to the mix proportions, in Table 1 was poured into the mould. Then, a plastic film was covered on the surface of the specimens to prevent the mixing water from evaporation. After 24 h, one copper wire was welded with the steel bar protruded from the end of the specimens. Subsequently, the prepared specimens were immersed in a saturated $Ca(OH)_2$ solution for 3 days. A steel corrosion apparatus is used to measure the anode polarization potential of the steel bars. When the test was to be conducted, the calomel electrode was connected with the copper wire, and the glass electrode was placed in the saturated $Ca(OH)_2$ solution as a reference. The potential values were recorded at 2, 6, 10 and 15 min.

2.2.3. The electrical resistance test of GHPC

Concrete specimens of $40 \times 40 \times 160$ mm^3, with two copper slices in the two long ends, were made according to the mix program (Table 2). The two copper slices were used as the measuring points of the ohmmeter. Unlike the speci-

Table 2
The experiment program and corresponding results

No.	Composite of binder pastes (%)				pH values of binder pastes in GHPC				Electrical resistance of concrete × 10 KΩ	50 Immersing–drying cycles		
										Mass-to-loss ratio of steel bars (%)	Apparent states of specimens	
	Cem	FA	SL	SF	3 days	7 days	28 days	120 days			Cracks or not	Crack width
1	100				12.688	12.678	12.965	12.681	12.00	5.92	Yes	Large
2	90			10	11.815	12.188	12.186	12.306	15.00	3.63	Yes	Small
3	90	10			12.025	12.206	12.341	12.144	9.29	6.69	Yes	Large
4	80	20			11.913	12.359	12.304	12.303	7.79	8.7	Yes	Large
5	70	30			11.583	12.471	12.671	12.683	7.29	11.91	Yes	Large
6	70		30		11.923	12.551	12.285	12.616	7.04	5.78	Yes	Medium
7	70	10	20		11.523	12.499	12.236	12.323	10.83	4.14	Yes	Small
8	60	30		10	12.006	12.176	12.268	12.325	37.91	3.73	No	/
9	60		30	10	11.974	12.227	12.337	12.324	45.36	4.53	No	/
10	60	10	20	10	11.020	12.158	12.107	12.077	17.38	2.57	No	/

Cem. denotes cement, FA denotes fly ash, SL denotes slag, SF denotes silica fume.

mens subjected to immersion–drying cycle test, these specimens that were performed electrical resistance test did not contain steel bars. After casting, these specimens were kept at room temperature for 24 h, then demoulded and cured for 28 days at 20 °C, relative humidity was 95 or greater. Three specimens were made for each batch, and the results were averaged. Before measuring the electrical resistance, these specimens were dried for 5 h at 50 °C. The electrical resistance of GHPC was measured using a digital ohmmeter with high-input impedance through the alternative current (AC) method.

2.2.4. pH value test of binder paste in GHPC

The binder paste at different ages was triturated until all of them passed through the sieve of 80 μm. Then, 5 g powder was added to 50 g distill water. After 2 h, the solution was filtrated. The pH value of the filtration solution was measured using a PXS-5 digital ion acidity meter supplied by Chen Du Apparatus Plant.

3. Experiment

3.1. Experiment program and results

The water-to-binder ratio for all these mixtures was 0.3. The dosage of the superplasticizer was 1.2 wt.% of binder with different types of mineral admixtures. The sand/(sand + stone) of concrete was 35%. The experiment program and corresponding results were listed in Table 2.

3.2. Analysis and discussion

3.2.1. pH values of binder pastes in GHPC

According to Table 2, the pH values of the pastes were obviously reduced after the addition of mineral admixtures to cement, especially at 3 days. This can be attributed to the fact that mineral admixtures absorbed some CH through the pozzolana reaction, and, in addition, the relative content of cement was also reduced when mineral admixtures were employed.

As for single-adding fly ash pastes, the pH values were reduced with an increase in the amount of fly ash at 3 days. However, the opposite phenomenon was found at 7, 28 and 120 days. This could be explained by the following facts:

(1) The addition of the fly ash diluted the concentration of Portland cement paste, increased the actual water-to-cement ratio and accelerated the rapid formation of CH.
(2) The relative amount of cement was reduced by the addition of fly ash; therefore, the amount of CH produced by the cement hydration was decreased.

At 3 days, Process (2) was more important than Process (1); thus, the amounts of CH and pH of pastes were reduced with the increase in the amount of fly ash. As time went on, Process (1) gradually overtook Process (2), as a result, the pH values of pastes containing a large amount of fly ash were higher than that of the pastes containing a low content of fly ash.

The following conclusions can be derived through the comparison of pH values of single-adding fly ash, slag and silica fume pastes:

(1) The pH value of single-adding silica fume paste was lower than that of single-adding fly ash before 28 days. The opposite result was found after 28 days. This came from the higher pozzolanic reactivity and rapid consumption of silica fume before 28 days, hence, the pH values of binder paste greatly decreased. However the pozzolanic reactivity of fly ash was gradually developed only after 28 days.
(2) The pH values of the single-adding slag paste was similar with that of the single-adding fly ash paste. It was very interesting to notice that a big fluctuation in pH values existed for single-adding slag paste from 7 to 28 days, which showed that the functions of slag and fly ash were very different in this period. This just confirmed that slag powder can react with CH at 7 days due to the higher early reactivity of slag powder than that of fly ash [6].

As for the double-adding binder pastes, the pH values of double-adding silica fume and fly ash (SF + FA) and double-adding silica fume and slag (SF + SL) were greater than that of double-adding fly ash and slag (FA + SL) at 3 days. The opposite result was correct at 7 days. The pH values of these three types of binder pastes were almost equal at 28 and 120 days. This could be explained by the following facts:

(1) At 3 days, the reduction in the relative cement content caused by the addition of mineral admixtures was more important than the acceleration of the cement hydration caused by the increase in actual water-to-cement ratio.
(2) At 7 days, the rapid pozzolanic reaction caused by the highest reactive silica fume overtook the reduction of relative cement content, which resulted in the pH values of double-adding samples containing silica fume (SF + FA and SF + SL) being lower than that of FA + SL.
(3) At 28 and 120 days, silica fume had been completely consumed, consequently, only fly ash and some slag were left. As we all know, the functions of fly ash and slag are similar after 28 days. As a result, almost equal pH values of SF + FA, SF + SL, FA + SL pastes were observed.

As for triple-adding binder paste (SF + FA + SL), pH values were lowest at all ages. This showed that the CH amount of SF + FA + SL could rapidly be consumed at all ages.

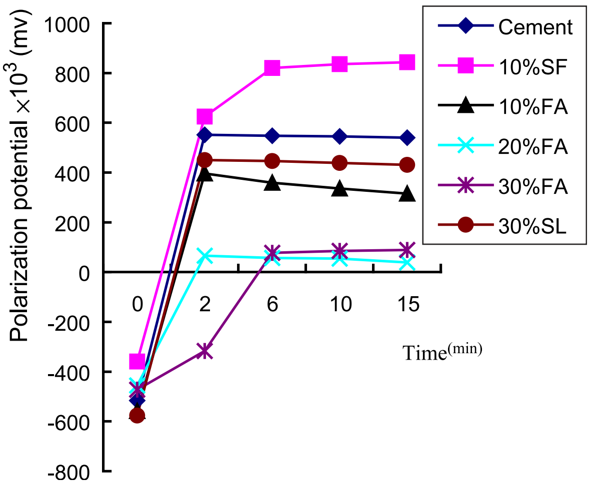

Fig. 1. Effects of types and amount of mineral admixtures on polarization potential.

According to the above analysis, when the mineral admixtures were added to the cement, the pH values of binder pastes were reduced, especially in the cases when two or three different mineral admixtures were added at the same time. Whereas, we could find that the pH values of all pastes beyond 3 days were still above 11.5, which were considered the critical breakage pH values of passivation film on the steel bar surface [7]. This showed that the dense passivation film could still form on the surface of steel bars in GHPC.

3.2.2. Electrical resistance of GHPC

From Table 2, we can see that after the addition of 10 wt.% of silica fume, the electrical resistance of concrete increased from 120 to 150 kΩ.

When fly ash or slag was added to the cement, the electrical resistance of concrete was reduced with the increase in the amount of fly ash or slag. It was very important to point out that the electrical resistance of concrete almost did not reduce any longer when the amount of fly ash exceeded 20%. For example, the electrical resistance of concrete with 20 wt.% of fly ash was 65% of that without mineral admixtures, while the electrical resistance of concrete with 30 wt.% of fly ash (7.29 kΩ) was almost equal to that with 20 wt.% of fly ash (7.79 kΩ).

Double- and triple-adding approaches markedly improved the electrical resistance of concrete, except of FA + SL. For example, the electrical resistance of concrete (SF + SL) reached 453.6 kΩ, which was 3.78 times greater than that of concrete without mineral admixtures.

According to the above analysis, double- and triple-adding approaches (SF + FA, SF + SL and SF + FA + SL) can greatly increase the electrical resistance of concrete. As we all know, the steel bar corrosion is caused by the electrochemistry reaction. The increase in the electrical resistance of concrete that reduced the corrosion current will reduce the electrical corrosion current, which may inhibit the electrochemical reaction. As a result, the steel bar corrosion reaction may be prevented or reduced.

3.2.3. Anode polarization potential of steel bar in hardened binder pastes

Anode polarization test can rapidly determine whether the binder pastes in concrete is damaged and what the degree of damage is. The following is the judgement criteria for anode polarization test [8]:

(1) The type of binder paste can be considered to be harmless to steel bars in concrete in the case that polarization potential rapidly moved towards the positive potential, and + 400 mV potential (vs. Ag/AgCl) is reached in 2 min, and the potential decrease is 50 mV or less in 15 min.
(2) The type of binder paste can be considered to be harmful to steel bars in concrete in the case that polarization potential slowly moved towards a positive potential and + 400 V potential is not reached in 2 min, or the potential decrease exceeds 50 mV in 15 min.

According to Figs. 1 and 2, the passivation film on steel bars in single-adding silica fume or slag paste maintained their integrity, while that in single-adding fly ash paste might be destroyed. According to the same principle, it was observed that the passivation film on steel bars in double- and triple-adding pastes was not destroyed.

3.2.4. Immersing-drying cycles

It can be seen from Table 2 that these steel bars embedded in concrete are rusted to some extent. According to the mass-to-loss ratios of steel bars, the addition of silica fume and slag, especially the former, showed a better resistance to steel corrosion, while the addition of fly ash led to the obvious decrease in the resistance to steel corrosion.

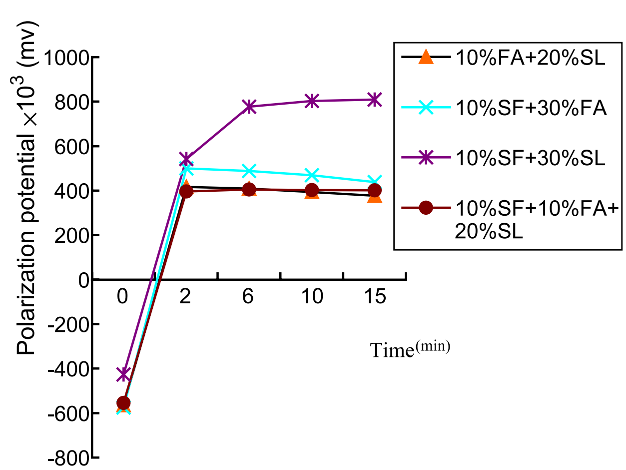

Fig. 2. Effects of adding approaches of mineral admixtures on polarization potential.

Double- and triple-adding approaches also showed a superior corrosion resistance to single fly-ash approach. This can be explained as follows:

(1) Using the different particle sizes of the three types of mineral admixtures, double- and triple-adding approaches optimized the particle distribution of binder pastes, which made the system of binder pastes denser.
(2) Double- and triple-adding approaches also greatly improved the transition zone between the cement and aggregate. As a result, H_2O and air do not easily penetrate into the concrete interior through the transition zone.

4. Conclusion

(1) The addition of mineral admixtures reduced the pH values of binder pastes in GHPC, especially in double- and triple-adding approaches, whereas the final pH values were still above the critical breakage pH values of passivation film on the steel bar surface (11.5).
(2) Double- and triple-adding mineral admixtures greatly increased the electrical resistance of concrete, with the exception of FA + SL, which might lead to a delay of the initial corrosion time of steel bars and a decrease of the corrosion rate.
(3) The results of electrochemistry and immerging–drying cycle tests indicated that single-adding silica fume or double- and triple-adding mineral admixtures possessed a superior resistance to the steel corrosion in GHPC.

Acknowledgements

The authors gratefully acknowledge the National Natural Science Foundation of China for financially supporting Project No. 59938170 and No. 50278018. The authors also thank Professor Hu Shuguan and Ding Qingjin for assistance and guiding.

References

[1] Z. Wu, Green high performance concrete—The development trend of concrete, Concr. Cem. Prod. (1) (1998) 3–5.
[2] H. Zhang, H.G. Wheat, M.L. Sennour, R.L. Carrasquillo, Corrosion of steel bars in concrete containing different chemical and mineral admixtures, Mater. Perform. 31 (12) (1992) 37–43.
[3] U. Takao, O. Ryo, I. Koichi, Y. Masaru, Corrosion behavior of steel bars embedded in fly ash concrete deteriorated by chlorides and carbonation, J. Soc. Mater. Sci., Jpn 49 (10) (2000) 1115–1120.
[4] K. Koichi, N. Shiro, H. Atsushi, M. Toyo, Steel corrosion in concrete with ground granulated blast furnace slag, J. Soc. Mater. Sci., Jpn 48 (8) (1999) 882–888.
[5] T. Kazuyuki, K. Mitsunori, A. Tokuro, M. Morihiro, Chloride permeability and corrosion of reinforcement in concrete containing silica fume, J. Soc. Mater. Sci., Jpn 40 (456) (1991) 1164–1170.
[6] Z. Yunsheng, Research on preparing high strength concrete in trip—adding mineral admixtures way, Chinese Build. Mater. Technol. (6) (1999) 16–18.
[7] H. Shuguang, Z. Houji, The serve life prediction of resistance steel bar corrosion concrete, J. Wuhan Univ. Technol. (4) (1997) 9–12.
[8] Transportation Ministry, The Test Methods of Port Concrete Engineering, Transportation Ministry Press, Beijing, 1981.