論文 A Study on the Corrosive Behavior of Steel Bars in Ecocement-Blast-Furnace Slag Mortars

Kwasi Osafo AMPADU *1 , Takashi KUBOTA *2 , Emi ITOH *3, Kazuyuki TORII*4

ABSTRACT Ecocement, which is a new type of hydraulic cement made from the incinerated ashes, contains large amounts of chlorides. Therefore, when this type of cement is applied to reinforced concrete structures, there is a risk of steel bar corrosion. In this study, the effect of the water to cement ratio and the replacement percentage of blastfurnace slag on the corrosion of steel bars embedded in ecocement-slag mortars under a severe saline environment was investigated. It was found that both the low water to binder ratio and the addition of slag could improve the corrosive behavior of steel bars embedded in the resulting mortars.
KEYWORDS: ecocement, incinerated ashes, blast-furnace slag, chloride ions, steel corrosion, linear polarization resistance, half cell potential, AC impedance

1. INTRODUCTION

In this experiment, the corrosion of mild steel bars embedded in ecocement mortars was studied in comparison to that of ordinary portland cement. Ecocement is a new type of hydraulic cement produced through the recycling of wastes. The New Energy and Industrial Technology Development Organization (NEDO) of Japan developed the technology for its manufacture [1]. However, the ecocement contains large amounts of chloride ions that are expected to accelerate the corrosion of steel bars if it is used in reinforced concrete structures. At present, its use has been limited to street pavements, concrete drains, sea defense blocks and other mass concrete structures. Blending the ecocement with blastfurnace slag is expected to improve the microstructure and chloride binding ability as in ordinary portland cement, when applied in reinforced concrete structures [2,3].

This experiment is therefore aimed at finding the effect of water to cement ratio and slag replacement percentage on the chloride induced corrosion of steel bars embedded in ecocement and OPC mortars.

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS, MIX PROPORTIONS AND SPECIMEN PREPARATION

Table 1 shows the chemical compositions of the ecocement (ECO), ordinary portland cement(OPC) and blastfurnace slag (SLAG) used in this experiment. The OPC was served as the reference.

*1 Department of Civil Engineering, Kanazawa University, Student, Member of JCI
*2 Department of Civil Engineering, Kanazawa University, Student
*3 Niken-Kogaku Co. Ltd, Researcher
*4 Department of Civil Engineering, Kanazawa University, Professor, Member of JCI

TABLE 1 Chemical Compositions of ecocement, OPC and blastfurnace slag (%).

	Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl
ECO	0.5	15.2	10.0	2.2	59.0	2.0	7.9	0.8	0	0.7
OPC	1.6	21.7	5.3	2.9	63.7	1.2	2.1	0.3	0.5	-
SLAG	1.6	32.2	13.3	0.7	42.3.	6.5	2.0	-	-	-

Mortar specimens were prepared with a cement:sand ratio of 1:2 (by mass) using standard sand. Specimen E1 (and O1 for OPC) was prepared with a water-binder (ECO or OPC plus SLAG) (W/B) ratio of 0.45. Specimens E2, E3, E4 (and O2, O3, O4 for OPC) were prepared at a W/B ratio of 0.55 and slag replacement ratios of 0%, 50% and 70% respectively. Specimens E5, E6, E7 (and O5, O6, O7 for OPC) were also prepared at a W/B of 0.65 and slag replacement ratios of 0%, 50% and 70% respectively. The fresh mortars were placed in a 160 mm by 100 mm by 60 mm rectangular mould with a 10mm diameter by 160 mm length mild steel and a stainless steel bars embedded at a cover depth of 10 mm. External stainless steel plugs were connected to one end of the steel bars to serve as contact points for electrical connection. Cylindrical specimens of 50 mm in diameter and 100 mm high were also cast for the measurement of chloride ion concentration profiles. The moulds were removed at 7 days after casting. The exposed surfaces were then coated with an epoxy resin leaving only the top surface uncoated in order to simulate one-dimensional chloride diffusion. The initial half cell potential and linear polarization resistance of the embedded mild steel bars were then measured every week. The specimens were then cured in a laboratory simulated severe saline environment consisting of a chamber in which 5% chloride solution is sprayed in an alternate 8-hour wet and 16-hour dry cycle at a constant temperature of 20°C. After the test, the specimens were split, and the corroded areas as well as weight loss of the embedded steel bars were measured. X-ray diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Differential Scanning Calorimetry (DSC) were also performed on the mortar samples around the steel bars.

2.2 ELECTROCHEMICAL MEASUREMENTS

The 3-electrode configuration technique was used for the LPR measurement. A saturated calomel electrode (SCE) was used as a reference electrode, whilst the embedded normal steel and stainless steel bars served as a working and auxiliary/counter electrode respectively. A DC of ± 20 mV was applied to polarize the working electrode from its rest potential. The corrosion current density, I_{corr} in μA/cm^2, was calculated using the Stearn-Geary equation, $I_{corr} = B/(A \bullet R_p)$ [4], where A is the surface area of steel bar and B, the Tafel constant, of 26 mV was used. After each measurement, the specimens were quickly returned into the curing chamber for the continuation of the spraying a 5% NaCl solution and drying cycle.

3. RESULTS AND DISCUSSION

3.1 LINEAR POLARIZATION RESISTANCE AND CORROSION CURRENT

Figs. 1 and 2 show the exposure time versus the corrosion current of the steel bar embedded in ecocement and OPC mortar specimens respectively. It is seen that for ecocement mortar specimens, the steel bars embedded in E2 (W/C = 0.55) maintain its passivity throughout the duration of the experiment, whilst that of E1 and E5 (W/C = 0.45 and 0.65) break down at exposure times of 14 and 12 weeks respectively. The corrosion current of steel bars embedded in E1 however started to decline after 30 weeks. On the other hand, in the case of OPC mortar specimens, the break down of passivity of the embedded bars in O2 and O5 (W/C =0.55 and 0.65) is at 13 and 14 weeks respectively, whilst that of O1 (W/C = 0.45) is maintained throughout the duration of the experiment.

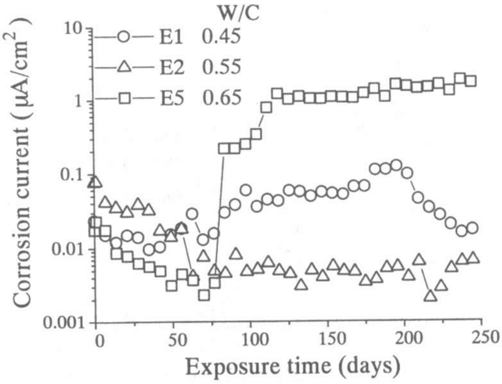

Fig. 1 Effect of W/C ratio on corrosion rate of steel bars in ecocement mortars without slag.

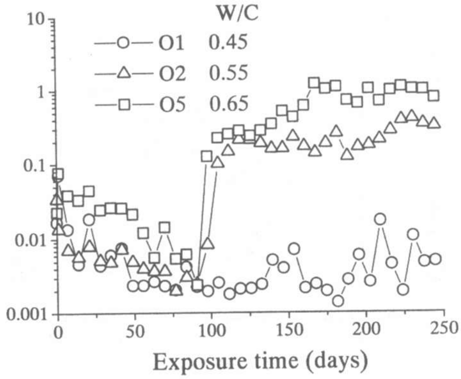

Fig. 2 Effect of W/C ratio on corrosion rate of steel bars in OPC mortars without slag.

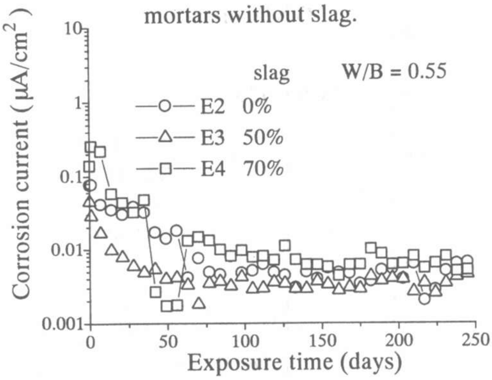

Fig. 3 Effect of slag on corrosion rate of steel bars in ecocement mortars with 0.55 W/B.

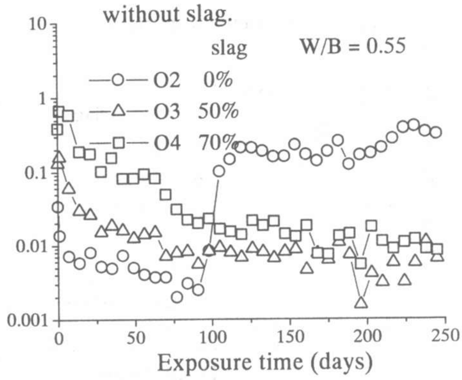

Fig. 4 Effect of slag on corrosion rate of steel bars in OPC mortars with 0.55 W/B.

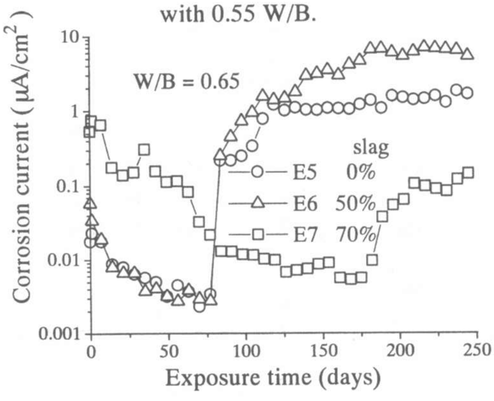

Fig. 5 Effect of slag on corrosion rate of steel bars in ecocement mortars with 0.65 W/B.

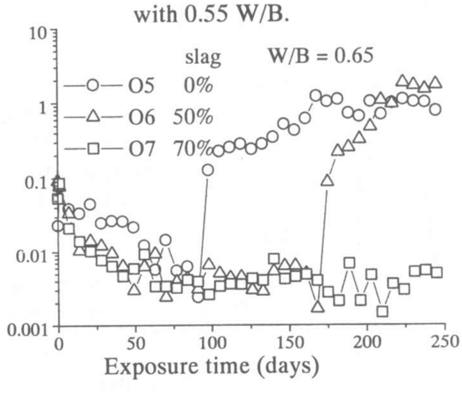

Fig. 6 Effect of slag on corrosion rate of steel bars in OPC mortars with 0.65 W/B.

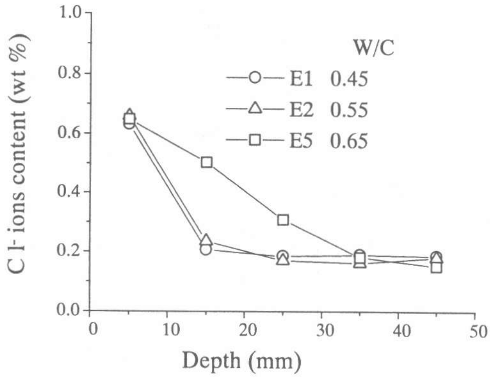

Fig. 7 Depth from mortar surface versus Cl ⁻ content of ecocement mortars.

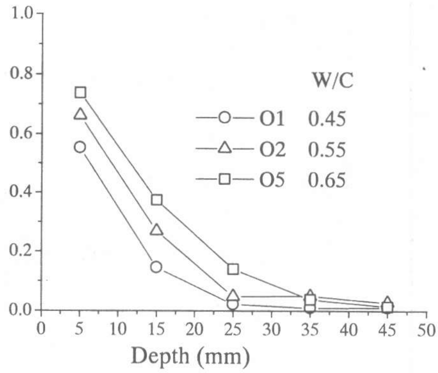

Fig. 8 Depth from mortar surface versus Cl ⁻ content of OPC mortars.

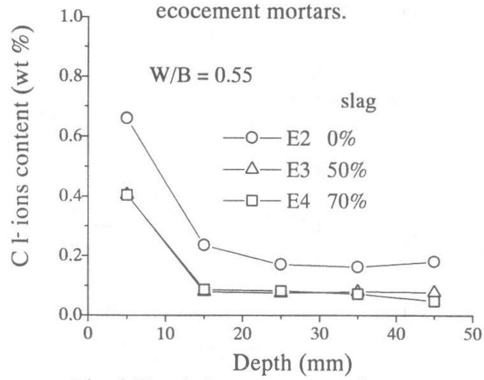

Fig. 9 Depth from mortar surface versus Cl ⁻ content of ecocement mortars with 0.55 W/B.

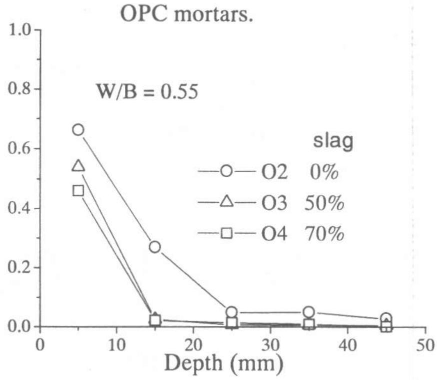

Fig. 10 Depth from mortar surface versus Cl ⁻ content of OPC mortars with 0.55 W/B.

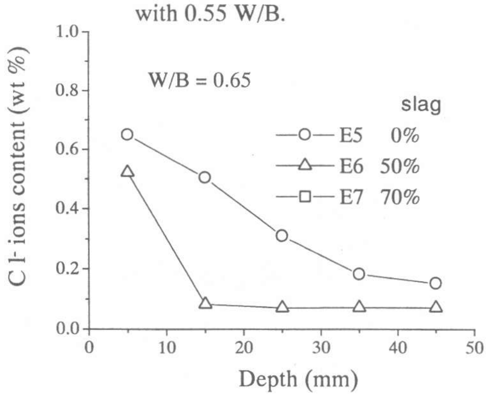

Fig. 11 Depth from mortar surface versus Cl ⁻ content of ecocement mortars with 0.65 W/B.

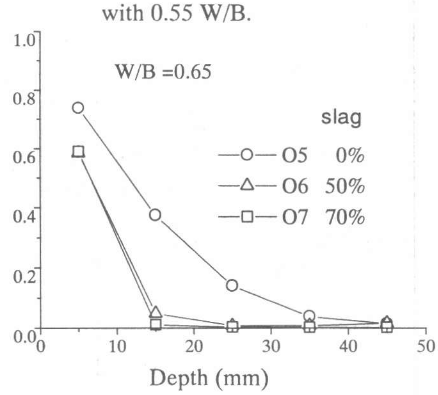

Fig. 12 Depth from mortar surface versus Cl ⁻ content of OPC mortars with 0.65 W/B.

Figs. 3 and 4 show the exposure time versus corrosion current of the steel bar embedded in ecocement and OPC mortars containing slag with a water to binder ratio of 0.55 in comparison to their mortar specimens without slag replacement (E2 and O2). It is seen that in ecocement mortar specimens, the corrosion current of the steel bars embedded in E3 and E4 (50% and 70% slag) and E2 (the control specimen) are almost the same and remained in the passive state throughout the duration of the experiment. On the other hand, for the corresponding OPC specimens, the passivity of the steel bars embedded in both O3 and O4 (50% and 70% slag) remained in the passive state throughout the duration of the experiment whilst that of O2 (the control specimen) lost passivity and corroded. O3 is however in a more passive state than O4

Figs. 5 and 6 show the exposure time versus the corrosion current of steel bars embedded in ecocement and OPC mortars containing slag with a water to binder ratio of 0.65, in comparison to the mortar specimens without slag replacement (E5 and O5). It is seen that 50% slag replacement do not result in an extension of the passivation period of the steel bar embedded in ecocement mortar containing slag, however, there is about 70% extension in the coresponding OPC specimen. On the other hand, 70% slag replacement in ecocement results in about 125% extension of the passivation period of the embedded steel bar, whilst in the case of OPC the passivity is maintained throughout the duration of the experiment.

3.2 CHLORIDE CONCENTRATION PROFILES IN MORTARS

Figs. 7 to 12 show the depth from mortar surface versus the chloride ion content of ecocement and OPC mortars with or without slag replacement to cement. It is clearly seen that for both ecocement and OPC mortars, the higher water to cement ratio gives the higher chloride ion content. However, there is virtually no difference between the chloride ion diffusion profiles of ecocement mortars with water to cement ratios of 0.45 and 0.55. Figs. 9, 10, 11 and 12, show that the addition of slag causes a significant reduction in the chloride ingress into both ecocement and OPC mortars. However, for ecocement mortars containing slag with a water to binder ratio of 0.55, there is not much difference between the chloride ion diffusion profiles of the mortars with slag replacements of 50% and 70%. The figure also shows that the chloride concentrations in the ecocement mortars are higher than those of the OPC mortars.

3.3 CALCIUM HYDROXIDE CONTENT AROUND STEEL BAR

The results obtained from DSC analysis of mortar samples taken around the steel bars indicate that the calcium hydroxide content in ecocement mortars is smaller than that in OPC mortars. Thus, the amount of pozolanic reaction in ecocement-slag mortars is expected to be lower in comparison to OPC. Microstructure improvement in ecocement-slag systems is therefore expected to be minimal. The pH of the pore solution of the ecocement mortars is also expected to be lower and hence offer minimal passivation effect in comparison to OPC.

3.4 WEIGHT LOSS AND CORRODED AREAS

Table 2 shows that the physical measurements such as weight loss and corroded area of steel bars in mortars agree very well with all the test results. It shows that for ecocement, the degree of corrosion of the steel bar embedded in mortars with a water to binder ratio of 0.55 (E2, E3 and E4) is the lowest. The degree of corrosion of the steel bars embedded in E3 and E4 are almost similar to that of OPC whilst the condition of the steel bar embedded in E2 is better than that of O2. The water to binder ratio affects the severity and extent of corrosion in OPC mortars as expected, but for ecocement mortars, the specimens with water to binder ratio of 0.55 performed better than that with water to binder ratio of 0.45. This anomalous behavior cannot be explained at this stage of the studies. It is worthy to mention that during mixing of the mortars, it was observed visually that the water demand for ecocement is higher than that of OPC.

TABLE 2 Weight loss and corroded area of steel bars after the corrosion test.

Specimen no.	W/B	Weight Loss (%)	Corroded Area (%)	Specimen no.	W/B	Weight Loss (%)	Corroded Area (%)
E1	0.45	0.3	13.1	O1	0.45	0.2	0.0
E2	0.55	0.2	4.5	O2	0.55	0.4	21.1
E3	0.55	0.2	4.1	O3	0.55	0.1	0.0
E4	0.55	0.2	1.2	O4	0.55	0.2	0.0
E5	0.65	0.7	23.5	O5	0.65	0.4	20.5
E6	0.65	2.8	54.9	O6	0.65	1.3	48.8
E7	0.65	0.4	10.4	O7	0.65	0.0	0.0

The table also shows that the corroded area of steel bars in the specimens of O6 and E6 (50% slag replacement) is greater extent than O5 and E5 (control specimens). It is worthy to note that the corrosion initiation of E5 and E6 occurred at the same time while that in O6 occurred later in time than O5 (see section 3.1). Also, the chloride level in O6 and E6 were lower than O5 and E5, respectively as described in section 3.2.

These results in combination with that of the DSC indicate that in slag-cement systems, the passivation period is extended, however, once the passive layer breaks down, the ensuing corrosion is much faster due to the low pH in the pore solution.

4. CONCLUSIONS

From the results of the experiment, the following conclusions were drawn;

(1) The addition of slag to ecocement provides an improvement with respect to resistance to chloride ingress and extension of the passivation period of steel bars if low to moderate water to binder ratio is used however at high water to binder ratio, a high percentage of slag replacement is required.

(2) In cement-slag systems with high water to binder ratio, there is an extension of the passivation period, but on breakdown of passivity, chloride induced corrosion proceeds at a faster rate, due to the lower content of calcium hydroxide in comparison to cement system without slag replacement.

It is worthy to mention that currently, two new types of ecocement, one with a low chloride content and the other with a high C_3A content, have been developed. The above investigations are ongoing for these cements and the results would be published in due course.

ACKNOWLEDGEMENTS

The authors give thanks to the ecocement project team of Taiheiyo cement corporation Ltd. for supplying the cement for the experiment.

REFERENCES

[1] Ono, Y., Ohmori, K., and Taguma, Y., "Ecocements Produced from Urban Garbage Incinerated Ash", Cement and Concrete, No. 586, pp.1-8, 1995 (in Japanese).

[2] Kawamura, M. and Torii, K., "Chloride Permeability of Concrete Containing a Fly ash and a Blast furnace Slag", Materials Research Soc. Symposium Proc., Vol. 137, pp.411-416, 1989.

[3] Dhir, R.K., EL Mohr, M.A.K and Dyer, T.D., "Chloride Binding in G.G.B.S. Concrete", Cement and Concrete Research, Vol. 26, No. 12, pp. 1767-1773, 1996.

[4] Stern, M. and Geary, A.L. "Electrochemical Polarization. I. A Theoretical Analysis of the Shape of Polarization Curves.", J. Electrochem. Soc., Vol. 104, pp. 56-63, 1957.