論文　Corrosive Behavior of Steel Bars Embedded in Cement Mortars Using Different Types of Ecocement

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ABSTRACT　In this study, the corrosive behavior of steel bars embedded in mortars made from two types of ecocement; high chloride type and low chloride type, blended with blast-furnace slag was investigated.　It was found that, in a severe saline environment, the degree of corrosion of steel bars embedded in plain mortars with low chloride type ecocement was lower than that with high chloride type ecocement, and that at low water to binder ratio, the addition of slag could improve the corrosive behavior of steel bars embedded in the mortars with both ecocements.

KEYWORDS: ecocement, incinerated ashes, blast-furnace slag, chloride ions, steel corrosion, linear polarization resistance, half cell potential, AC impedance

1.　INTRODUCTION

　　　　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 incinerated ashes contain large amounts of chloride, which, if not removed during the production process, is expected to accelerate the corrosion of steel bars in reinforced concrete structures [2].　In the production process, the chloride could be removed but at a high cost.　In the first series of ecocement that were produced, the chlorides were not removed resulting in a high chloride type ecocement (type I).　Its use was limited to street pavements, concrete drains, sea defense blocks and other mass concrete structures. As an improvement over the type I, a second type of ecocement with low chloride content (type II) has now been produced but at a higher cost than that of type I.

　　　　In this experiment, the corrosion of mild steel bars embedded in high chloride type ecocement (type I) mortars were studied in comparison to that of low chloride type ecocement (type II).　The beneficial effects of slag, especially chloride binding and microstructure structure improvement, on both types of ecocement were also investigated [3].

2. EXPERIMENTAL PROCEDURES

2.1 MATERIALS, MIX PROPORTIONS AND SPECIMEN PREPARATION

　　　　Table 1 shows the chemical compositions of type I and type II ecocement and blast-furnace slag used in this experiment.　The essential difference between the mineral compositions of type I and type II ecocement in comparison to OPC is that type II is quite close to OPC in chemical compositions while type I has higher Calcium Chloro-Aluminate ($C_{11}A_7CaCl_2$), Alite (C_3S) and Calcium Sulfate ($CaSO_4$) than type II (and OPC).

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TABLE 1 Chemical Compositions of type I and type II ecocement (%)

	Ig. loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Cl
ECO I	0.5	14.9	10.5	2.5	56.7	1.7	9.2	0.8	0.01	0.80
ECO II	0.6	18.0	8.8	2.5	62.1	1.7	3.7	0.3	0.01	0.08
SLAG	1.6	32.2	13.3	0.7	42.3.	6.5	2.0	-	-	-

The quantity of sulfate present in type I ecocement affects the hydration characteristics of Calcium Chloro- Aluminate during cement hydration. Low sulfate content results in the formation of monosulfo- aluminate as the preferred hydration product while too much sulfate results in the formation of ettringite and secondary gypsum as the hydration products of Calcium Chloro- Aluminate. The formation of these products has the consequence of increased water demand. In type I ecocement, ettringite and secondary gypsum are expected to be the preferred hydration products as opposed to monosulfo- aluminate whilst in type II the opposite is expected. It was observed during a trial mix of the mortars that type I sets rapidly while type II has a normal setting behavior. The water demand for type I was also found to be higher than type II. A retarder was therefore used during the preparation of the type I mortars.

Mortar specimens were prepared with a standard sand at a cement:sand ratio of 1:2. Specimens I- 1 and II- 1 were prepared with a w/c ratio of 0.45. Specimens I- 2, I- 3, I- 4 for type I (and II- 2, II- 3, II- 4 for type II) were prepared at a w/b ratio of 0.55 and slag replacement ratios of 0%, 50% and 70% respectively. Specimens I- 5, I- 6, I- 7 (and II- 5, II- 6, II- 7 for type II) 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 rods 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 rods were measured and following that the specimens were placed in an environmental chamber of severe saline conditions. The half- cell potential and linear polarization resistance measurements were taken every week while AC impedance measurements were also taken monthly for a total period of 273 days. At the end of the exposure period, 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. The cylindrical specimens were sliced into 10mm discs and used to measure the chloride concentration profiles in accordance to the JCI- SC5 standard method of measurement.

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 $\pm$ 20 mV was applied to polarize the working electrode from its rest potential. The corrosion current density, I_{corr} in $\mu A/cm^2$, 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 at 20 $^\circ$C.

3. RESULTS AND DISCUSSION

3.1 LINEAR POLARIZATION RESISTANCE AND CORROSION CURRENT

Fig. 1 A, C and **E** show the variations of corrosion current with exposure time for the type I specimens. It is seen in **Fig. 1 A** that, the water to cement ratio does not have any appreciable effect on the corrosion rate of the steel bars embedded in the mortar specimens, contrary to normal cement behavior [2]. **Fig 1 C** shows that at a water to binder ratio of 0.55, the higher the slag replacement ratio, the lower the corrosion current. On the other hand, at water to binder ratio of 0.65, the specimen with 50% slag replacement, I- 6, ended up with a corrosion current higher than the control specimen, I- 5. The specimen with 70 % slag replacement, I- 7, however resulted in lower corrosion current as at the end of the exposure period of 273 days.

Fig. 1 B, D and **F** show the variations of corrosion current with exposure time for the type II specimens. **Fig. 1B** shows that, the corrosion current of the specimen with water to cement ratio of 0.45 is much lower than that of the specimen with water to cement ratios of 0.55 and 0.65 during the corrosion test. **Fig. 1 D** shows that at a water to binder ratio of 0.55, during the initial 203 days of exposure, the higher the slag replacement ratio, the lower the corrosion current, however after this period, the corrosion rate of the steel bar embedded in the specimen with 50% slag replacement, II- 3, started to accelerate, by passing the control specimen (II- 2) as at the end of the exposure period of 273 days. On the other hand, the steel bar embedded in the mortar with 70% slag replacement (II-4), remained at a low corrosion current till the end of the exposure period. **Fig. 1 F** also shows that at a water to binder ratio of 0.65, slag replacement rather resulted in higher corrosion current, especially the specimen with 50% slag replacement, (II- 6).
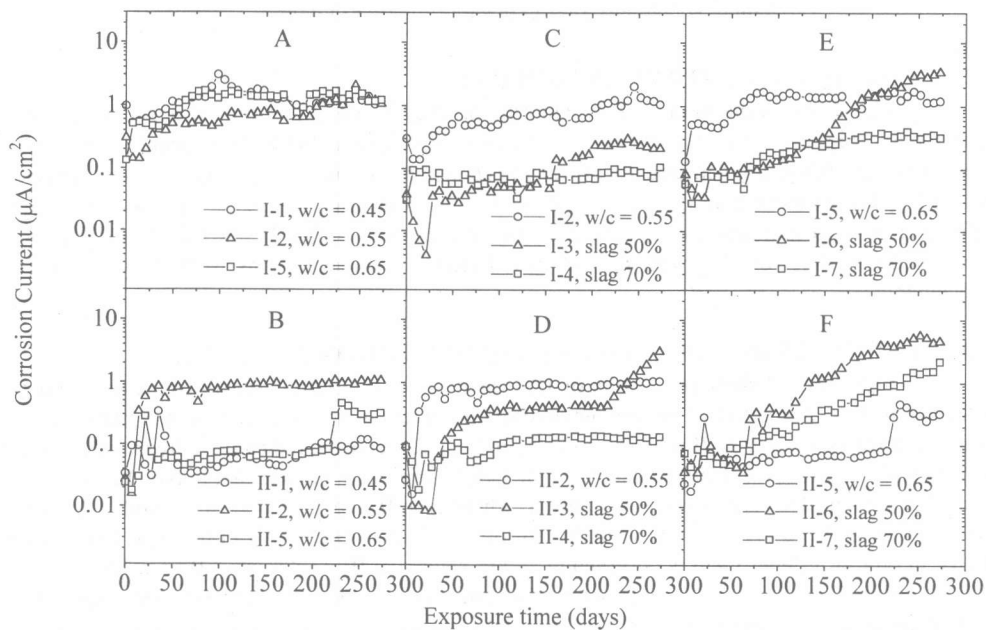

Fig. 1 Corrosion current versus exposure time
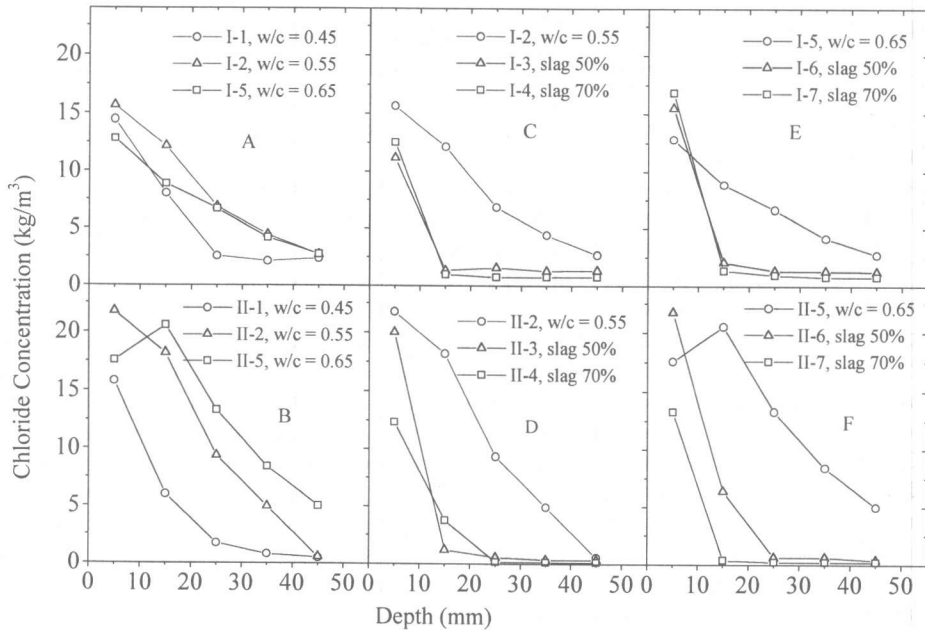for type I and II ecocement specimens

Fig. 2 Chloride ion concentration versus depth for type I and II
ecocement specimens after exposure time of 273 days

3.2 CHLORIDE CONCENTRATION PROFILES

Fig. 2 shows the graphs of the chloride profiles in type I and type II ecocement mortar specimens. **Fig. 2A** shows that, for type I mortar specimens, the chloride ion concentration profiles were not much different independently of water to cement ratio, contrary to normal cement behavior, whilst **Fig 2B** shows that, in the case of type II mortar specimens, the higher the water to cement ratio the higher the chloride content as occurs in normal cement. **Figs. 2C, D, E** and **F** clearly show the beneficial effect of slag with respect to chloride ion concentrations in both type I and II ecocements.
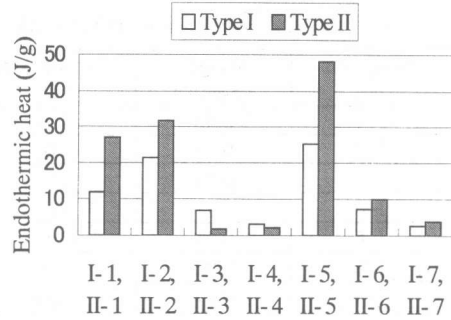
3.3 CALCIUM HYDROXIDE CONTENT AND HYDRATION PRODUCTS

Figs.3 and **4** show the results of DSC analysis of the mortar specimens taken from the different depths. It is seen that the calcium hydroxide content in type I ecocement mortars is smaller than the corresponding type II mortars, and also in both ecocements, the calcium hydroxide content significantly decreases with slag content. The DSC curves also indicate that in type I mortars, the ettringite content decreases with slag addition, whilst type II gives the opposite result. Also, the DSC curves indicate that, there is virtually no formation of Friedel's salt in the type I specimens whilst in type II, Friedel's salt is observed in all but specimen II- 7 (70% slag, 0.65 w/b).

Fig. 5 shows the X- ray diffraction diagrams of type I and II ecocement mortar specimens with water to cement ratio of 0.55. It is seen that the intensity of the ettringite peak is higher in type I than in type II whilst that of monosulfo- aluminate hydrate is higher in type II than in type I as expected. The calcium hydroxide peaks in both type I and II ecocement are of the same intensity in contrast to the DSC results.
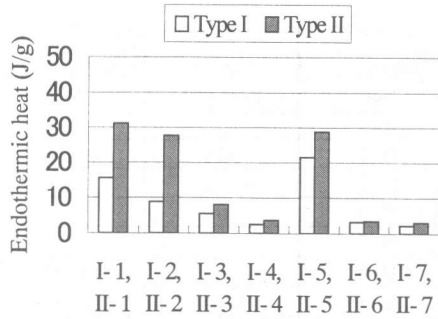
Fig.3 Calcium hydroxide content obtained from DSC analysis of type I and II mortars (10-20 mm depth)

Fig.4 Calcium hydroxide content obtained from DSC analysis of type I and II mortars (40-50 mm depth)

2θ degrees (Cu - Kα)
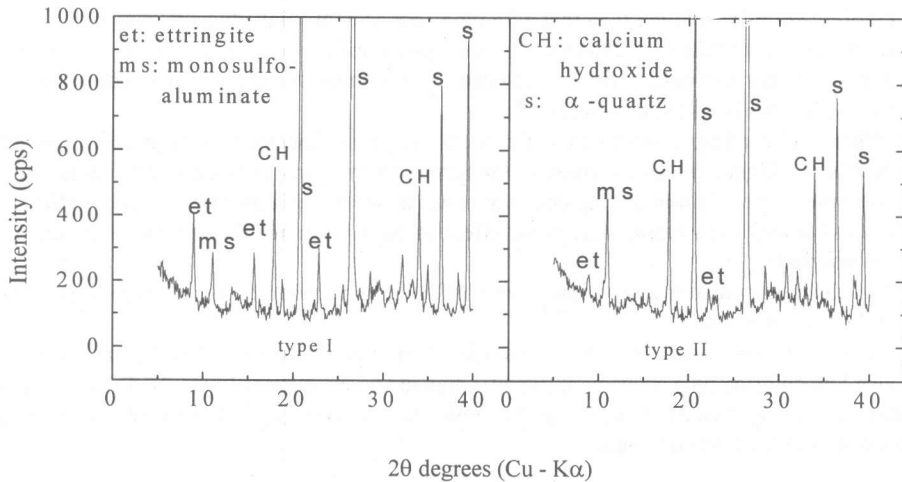
Fig. 5 X-ray diffraction curves for type I and II ecocement specimens with water to cement ratio of 0.55 at the exposure time of 273 days.

3.4 WEIGHT LOSS AND CORRODED AREAS

Table 2 shows the results of the physical measurements; weight loss and corroded area of the steel bars. It is seen that for type II specimens, II- 3 (50% slag, w/b=0.55) suffered the most severe corrosion, followed by II- 6 (50% slag, w/b=0.65) and II- 7 (70% slag, w/b=0.65), which is in agreement with the results of the electrochemical measurements. In fact, a closer look at the other figures in the table confirms that the physical measurements validate the electrochemical measurements. Another important observation is that, the corrosion current of all the specimens with zero weight loss and corroded area are all less than 0.1 $\mu A/cm^2$ while a very severe corrosion along with pitting has occurred in the specimens with corrosion current of more than 1$\mu A/cm^2$ which agrees very well with the criteria relating corrosion current to corrosion rate [5].

The overall results indicate that, when both ecocements are blended with slag, there is actually microstructure improvement, however, due to the low content of calcium hydroxide around the steel bars, the [Cl^-/OH^-] ratio in pore solution quickly becomes high once chlorides diffuse to the steel bar in the mortar in a severe saline environment.

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

Specimen no.	Weight Loss (%)	Corroded Area (%)	Specimen no.	Weight Loss (%)	Corroded Area (%)
I- 1	0.33	24.49	II- 1	0	0
I- 2	0.41	16.07	II- 2	0.14	15.78
I- 3	0.09	1.58	II- 3	0.78	42.74
I- 4	0	0	II- 4	0	0
I- 5	0.41	30.66	II- 5	0	0
I- 6	0.92	45.99	II- 6	0.66	37.50
I- 7	0.01	21.34	II- 7	0.44	34.52

4. CONCLUSIONS

From the results of the experiment of the corrosion test for ecocement mortars, the following conclusions were drawn;

(1) The degree of corrosion of steel bars embedded in the plain mortars with type II ecocement (low chloride content) is lower than that with type I ecocement (high chloride content).

(2) In the mortars of both high chloride type and low chloride type ecocements, large amount of slag and low water to binder ratio are required for any improvement with respect to corrosion of embedded steel bars to be manifested.

(3) When slag is added to both types of ecocement, type I ecocement performs better than type II despite the higher chloride content of the former in comparison to the latter. In fact in type II ecocement, the addition of slag does not result in any significant improvement with respect to corrosion and even cause a negative effect at high water to binder ratio in a severe saline environment.

(4) The electrochemical measurement is very effective in the monitoring of corrosion of steel bars embedded in mortar.

The extra cost incurred in the extraction of chloride from the incinerated ashes in order to produce low chloride type ecocement (type II) may not be economically justified since the resulting cement is not significantly better than the high chloride type (type I) with respect to corrosion resistance of embedded steel bars.

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