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A Study on Durability of Blast Furnace Slag Cement Concrete Mixed With Metakaolin-Based Artificial Pozzolan in Actual Marine Environment

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ABSTRACT

The study focuses on a new material called Metakaolin, which is an industrial by-product. The concrete using Ground Granulated Blast Furnace Slag (GGBS) has some disadvantages like as lower initial strength and higher dry shrinkage. In the previous study, concrete using Metakaolin with GGBS has been confirmed to improve the performance of GGBS concrete without compromising the durability aspects (Eguchi, 2011). However, concrete with both Metakaolin and GGBS have not been studied under actual environment. Therefore, in this study, long term durability of concrete made with Metakaolin and GGBS under marine environment has been investigated. From the experimental results, it is found that GGBS concrete with Metakaolin has good resistance against chloride ingress when compared to GGBS concrete even though the resistance against carbonation is lowered slightly in actual environmental conditions.

Keywords. Metakaolin, Ground Granulated Blast Furnace Slag, Marine Environment, Chloride Penetration, Carbonation.

1. INTRODUCTION

Recently, increasing CO_2 amount discharged to the atmosphere due to human activity, which causes global warming and climatic changes, has been a wide concern. Therefore, construction industry is strongly recommended to use industrial waste, such as blast furnace slag and fly ash more effectively to reduce CO_2 emissions. Author's previous research reported that concrete using GGBS cement which consists of ground granulated blast furnace slag and ordinary Portland cement has high resistance to chloride attack, chemical erosion and other deteriorations (Matsumoto, 2009). On the other hand, GGBS concrete has some disadvantages comparing to ordinary Portland cement concrete, such as lower initial strength and higher dry shrinkage. Therefore, for wider use of GGBS in the construction field of concrete structures, it is necessary to avoid such problems.

In order to solve those problems, blast furnace fume (here in after called "BFF") was firstly tried to examined in our research works. BFF is obtained by collecting the gas discharged from small blast furnaces in China. It has reactivity like as pozzolan, which can be expected to generate Calcium Silicate Hydrates and Calcium Aluminate Hydrates by its rapid reaction with $Ca(OH)_2$ in GGBS concrete during early age. According to previous experimental results, it is possible to improve not only the initial strength (Numata, 2007) but also resistance against chloride penetration of GGBS concrete by adding BFF (Umeki, 2009). However, continuous produce of BFF cannot be expected anymore, because of reduction of the gas emission from the blast furnaces in China due to recent modernization of the system.

Recently, as an alternative material to BFF, an artificial pozzolan material made of coal mines and coal ash, etc. ,which has similar characteristic to BFF, has been developed. This material is called Metakaolin-based artificial pozzolan (here in after called as “Metakaolin”). This material has been produced in Japan and growth in demand can be expected in the future. In this study, the long-term durability for three years exposure to actual marine environment has been examined with concretes made of ordinary Portland cement, ground granulated blast furnace slag and Metakaolin.

2. OUTLINE OF EXPERIMENT

2.1 Properties of Metakaolin

Table 1 shows the density and specific surface area of Metakaolin , GGBS and OPC used in this study. Comparing to GGBS, Metakaolin is finer material having lesser density and larger specific surface area. Table 2 shows the chemical composition of Metakaolin. Metakaolin has almost similar chemical characteristic to OPC and GGBS, but having a higher content of SiO_2 and Al_2O_3.

Table 1. Physical property of Metakaolin

	Density (g/cm^3)	Specific surface area (cm^2/g)
Metakaolin	2.70	7309
GGBS	2.90	4189
OPC	3.15	3370

Table 2. Chemical composition (mass (%))

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Metakaolin	36.60	14.70	1.95	31.00	8.73	4.75
GGBS	22.70	14.20	0.43	46.80	0.33	1.76
OPC	20.99	5.26	2.67	65.21	2.13	2.05

2.2 Overview of specimen

Table 3 shows the mix proportions used in the experiment. Water binder ratio (here-in-after called “W/B”), fine aggregate ratio, and water content were kept constant for all mix

Table 3. Mix proportion

W/B (%)	s/a (%)	Mixing ratio of binder	Unit weight(kg/m^3)							Slump value (cm)
		C:GGBS:MKP	W	C	GGBS	MKP	S	G	SP (%)	
50	45	OPC	175	350	−	−	815	1000	0.18	8.5
		BB		175	175	−	810	993	0.15	9.5
		C40:B40:M20		140	140	70	806	989	0.18	9.5
		C20:B40:M40		70	140	140	802	984	0.22	9.5
		C20:B60:M20		70	210	70	804	987	0.18	9.0

*C:Ordinary Portland cement, B:Ground Granulated Blast Furnace Slag, M:Metakaolin-based artificial Pozzolan
For Ex: C40 - 40% Cement content

proportions, and poly-carboxylic super-plasticizer (SP) was used to adjust target slump of 10 ± 2cm. Binders used for concrete are, Metakaolin, ordinary Portland cement and GGBS. As for aggregate, river sand from Fuji River is used as fine aggregate (density of 2.61g/cm^3 and water absorption of 1.76%) and crushed stone from Kagoshima prefecture is used as coarse aggregate (density of 2.62g/cm^3, water absorption of 0.93% and maximum size of 20mm). Roughly, 3 types of concrete are prepared according to binder material. First type is OPC concrete which used only ordinary Portland cement as binder to make concrete. Second type is BB concrete which is made with binders including both ordinary Portland cement and GGBS with equal amounts in weight. Third type is Metakaolin concrete which introduces Metakaolin as binder addition to OPC and GGBS. In Metakaolin concrete, several mix proportions were prepared with the different replacement ratios. One is concrete made with the binder including 20% of Metakaolin, and 40 % of OPC and GGBS respectively. Other two are concretes made with binders in which OPC : GGBS : Metakaolin ratio are 20:60:20 and 20:40:40 respectively. Here, Metakaolin, of which 5% is replaced with anhydrous gypsum as stimulant, was used in the experiment.

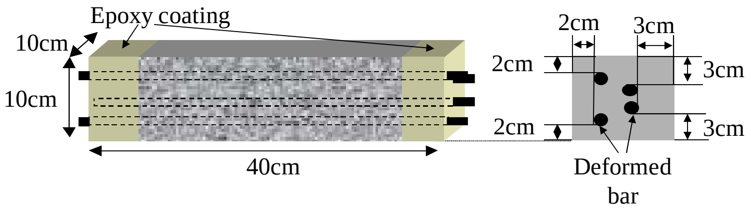


Figure 1. Specimen for durability test

Figure 1 shows the specimen shape. 10*10*40cm prism specimens with 4 deformed bars of which 2 are embedded at 2cm of cover thicknesses and other 2 bars at 3cm. Both ends of specimen are coated with Epoxy resin. For compressive strength test, cylindrical specimens with 10cm in diameter and 20cm in length are prepared.

2.3 Exposure environment

The specimens are exposed in two zones, namely, submersed and tidal zone, located in Taniyama Port in Kagoshima Prefecture, Japan. A stage of submersed zone is in the level of - 0.8m relative to LWL, where submerged in the sea water throughout the year. A stage of tidal zone is in the level +1.5m relative to the LWL, where subjected to wet and dry condition due to tides. Exposure period is scheduled for 5 years. However, in this paper, the examinations are carried out based on the exposure tests results up to 3 years in both zones.

2.4 Outline of experiments

(1) Compressive strength

Cylindrical specimens are cured in the normal water with 20 ^{o}C for 28 days and then cured in air for 1 month before exposing the specimens to actual marine environment for 1, 3 and 5 years. After each exposure period, compressive strength test of the specimens is carried out, in accordance with JIS A 1108 - 2006.

(2) Pore distribution

The prism specimen for durability test is also subjected to same environmental conditions. Small concrete samples taken from the exposed specimens are collected at a depth of 2-3cm from the surface of the specimen and analysed for pore size distribution in concrete. The test method is based on mercury intrusion porosimetry.

(3) Carbonation progress

At the exposure periods of 1 year and 3 years, the prism specimens exposed in the marine environments are split longitudinally along rebar and then carbonation depth of concrete is measured by phenolphthalein method. In addition, an method to estimate the pH distribution in concrete is carried out. Fine powder which size is under 150μm is collected from specimens at each predetermined depth, then 0.35g of powder is stirred for 24 hours in 30g distilled water. Stirred solution is used to measure pH value by using pH electrode.

(4) Chloride penetration

Fine concrete powder screened under 150μm sieve is collected from the specimens at each predetermined depth.. The powder is used for determining the total amount of chloride content in concrete at each predetermined depth in accordance with JCI-SC5. Apparent chloride ion diffusion coefficient is also calculated based on Fick’s second law in accordance with JSCE - G572 - 2003.

(5) Rebar corrosion

At the end of each predetermined exposure period, rebars were taken out carefully from specimens to measure corrosion area of rebar. In the measurement, a transparent film is attached on the corrosion area. Then, the area is sketched on the film and scanned for image processing for obtaining corrosion area.

3. RESULTS AND DISCUSSION

(1) Compressive strength

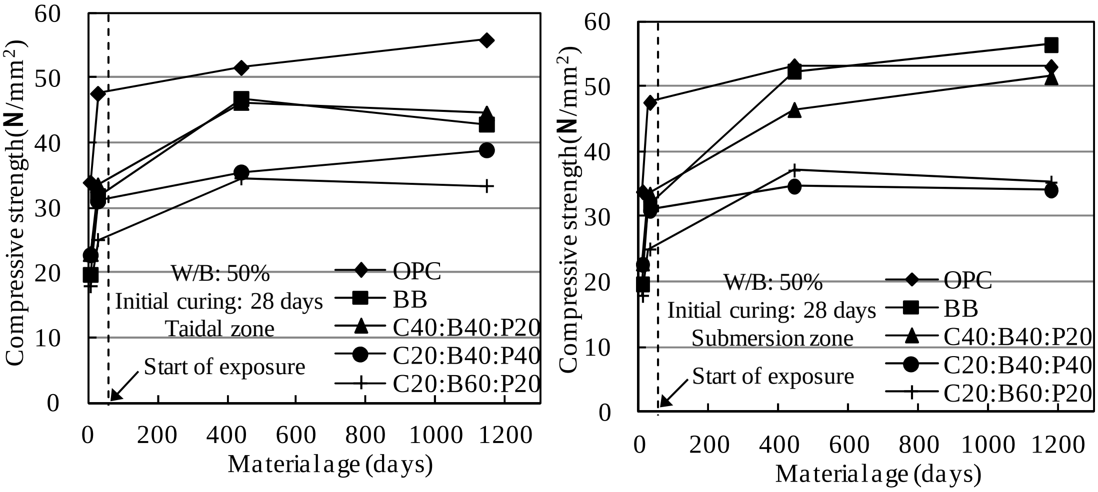


Figure 2. Compressive strength

Figure 2 shows the change of compressive strength with time for the concrete exposed to tidal and submersed zone. After 7days of normal water curing, the compressive strength of concrete with Metakaolin is slightly higher compared to BB concrete. In case of specimens exposured to tidal zone, BB concretes and concretes with Metakaolin show the lower of long term strength compared to OPC, though the strength of C40:B40:M20 specimen is almost the same as BB. In case of concrete under Submersed zone, however, compressive strength of Metakaolin concrete with C40:B40:M20 of binder ratio shows increasing long term strength and is similar to OPC and BB.

(2) Pore distribution

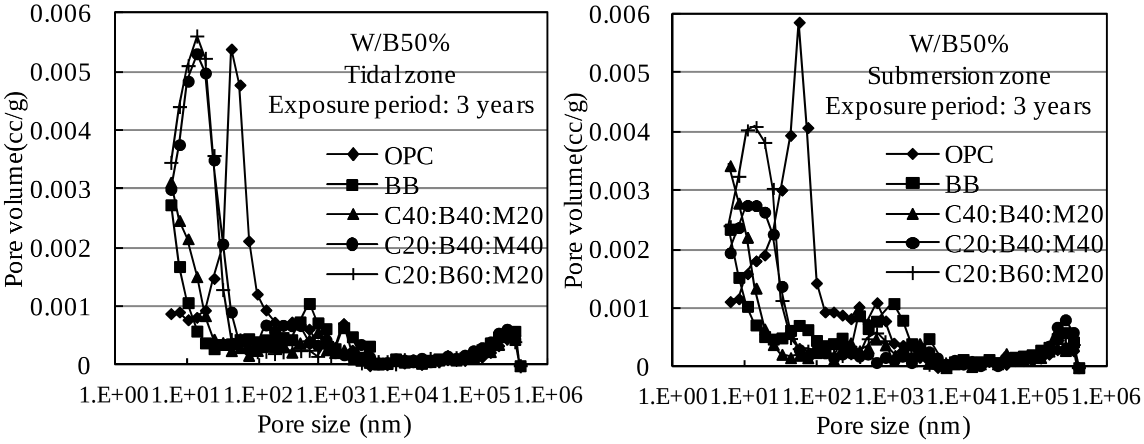


Figure 3. Pore size distribution

Figure 3 shows the distribution of the internal pores of concrete after 3 years of exposure. OPC concrete have the highest peak at the pore diameter of about 100nm. BB concrete have peak around 10nm and secondary peak at the pore size of about 1000nm. On the other hand, Metakaolin concrete have peak at pore size of 10nm and almost no peak at larger pore sizes. The secondary peak at larger pore size of BB concrete has been reduced by using Metakaolin. Concrete mixed with Metakaolin has been confirmed to have very fine pores. Long term pozzolanic reaction of Metakaolin causes densification of concrete. The dense concrete is expected to have high resistance against chloride penetration.

(3) Carbonation progress

Figure 4 shows the carbonation depth of specimens exposed to tidal zone and submersed zone for exposure periods of 1 year and 3 years. The concrete in tidal zone has carbonated more than the ones in submersed zone. And also specimens exposed for 3 years have the lager carbonation compared to the one for 1 year exposing. Concretes using Metakaolin have

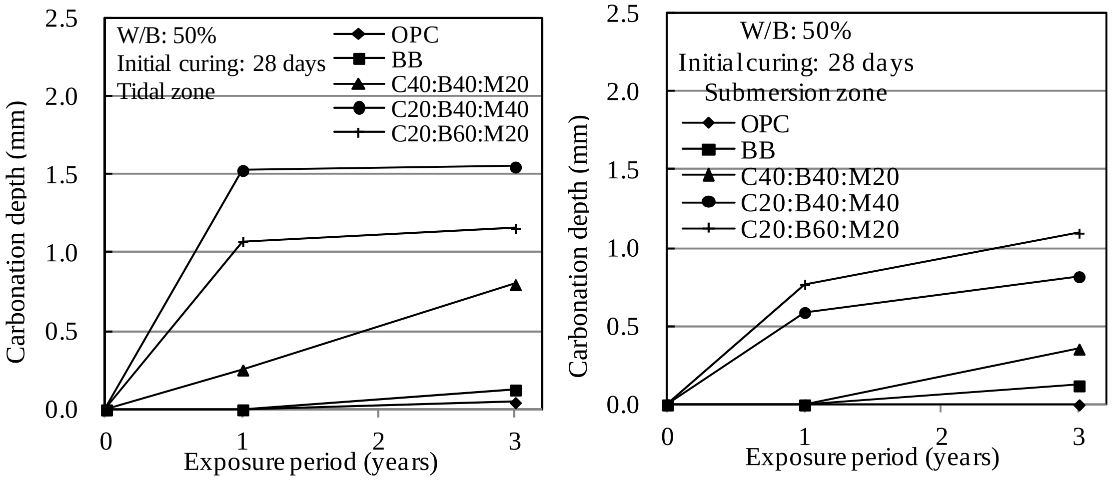


Figure 4. Carbonation depth

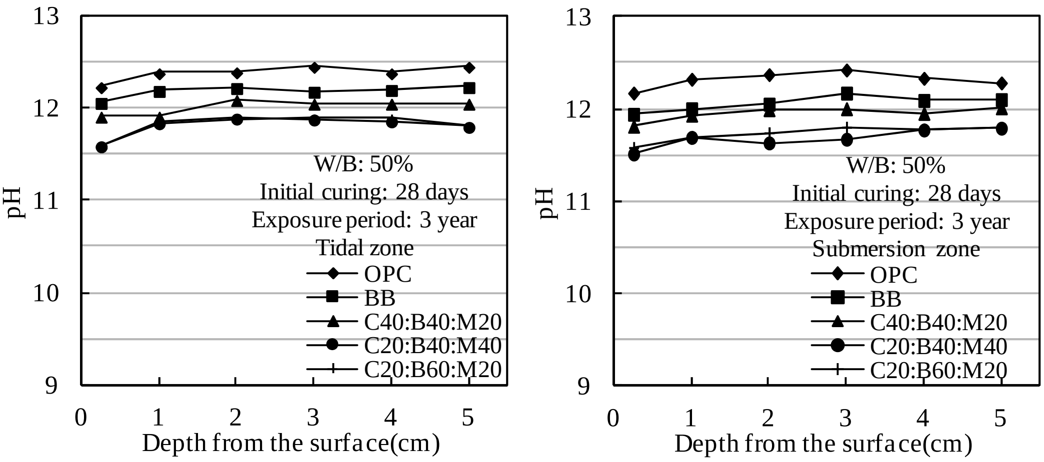


Figure 5. Internal pH of the specimen

high carbonation depth compared to BB and OPC even though the carbonation depth has not reached to 2mm depth from the surface.

Figure 5 shows the pH distribution in concretes exposed to tidal zone and submersed zone after 3 years of exposure. Though each type of concretes in the both marine environments have similar pH value distributions, Metakaolin concretes have lower pH values when compared to OPC. At depths of 2cm and 3cm, Metakaolin concrete of C20:B40:M40 and C20:B60:M20 have pH values of 11.6- 11.8, while OPC concrete and BB one have about 12.4 and 12.0-12.2, respectively.

(4) Chloride penetration

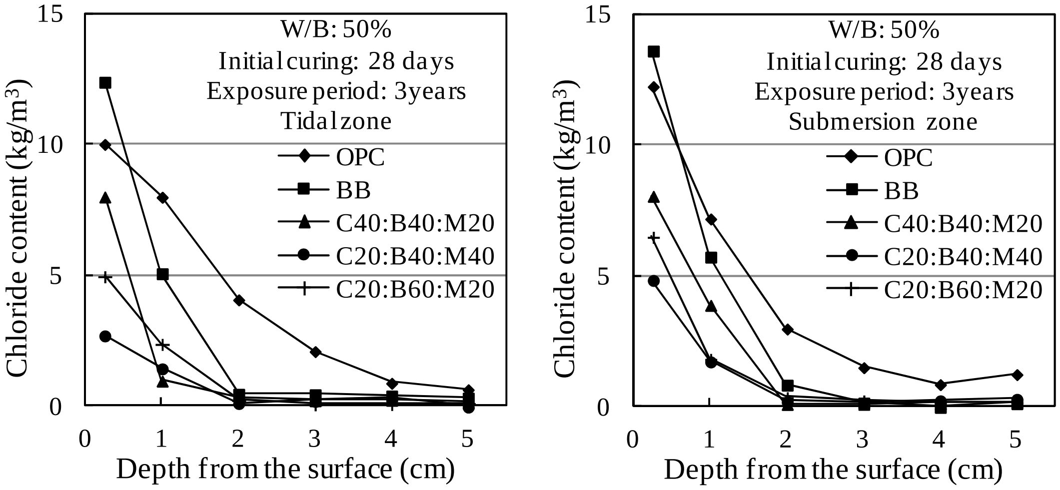


Figure 6. Profiles of chloride content in concrete

Figure 6 shows profiles of total chloride ion content in all types of concretes exposed to tidal or submersed zone for 3 years. In the tidal zone, OPC concrete has 4.10kg/m^3 of chloride content at depth of 2cm and 2.13kg/m^3 at 3cm depth, while in submersed zone, these are 3.01kg/m^3 at 2cm depth and 1.54kg/m^3 at 3cm depth. These mean that at rebar positions where are 2cm and 3cm of cover thickness, the total chloride ion content in OPC concrete seems to be over the threshold level for corrosion initiation. On the other hand, total chloride ions are highly concentrated around surface of BB concrete and almost no chloride content at depths greater than 2cm. These results match with the past researches where BB concrete had high resistance to chloride ingress than OPC one (Matsumoto, 2009). In the case of Metakaolin concretes, the total chloride ion in concrete near the surface is lesser compared to BB, but has similar trend to BB with almost no chloride content at the depth more than 2cm. Especially, the total chloride ions in Metakaolin concretes of C20:B40:M40 and C20:B60:M20 are less compared to BB one. Therefore, the concretes with GGBS+Metakaolin are confirmed to have higher resistance against chloride ingress compared to BB concrete.

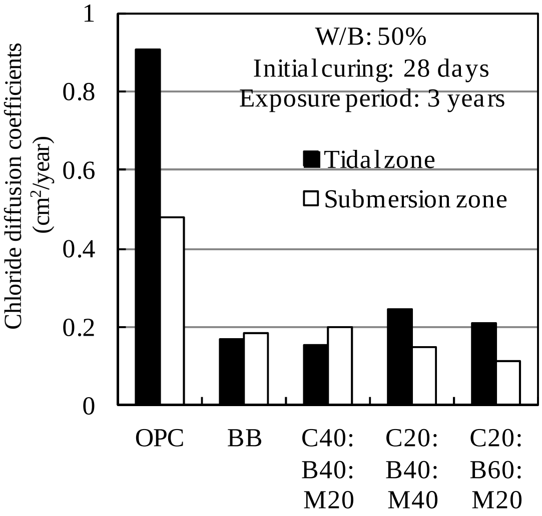


Figure 7. Apparent chloride diffusion coefficients

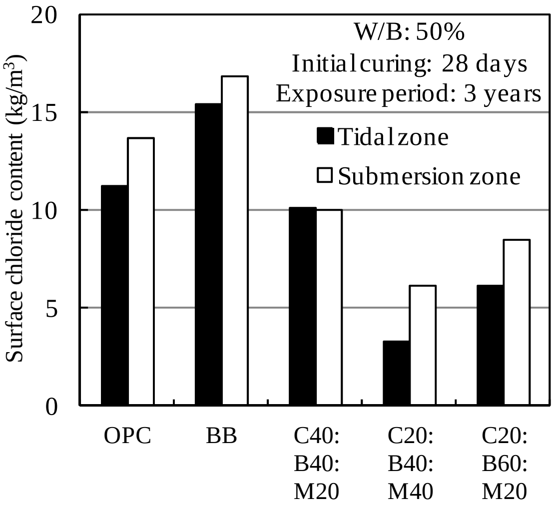
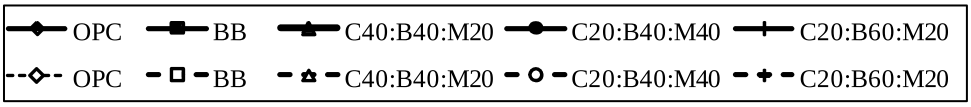


Figure 8. Surface chloride content

Figure 7 shows the apparent chloride diffusion coefficient of all types of concretes in tidal zone and submersed zone for 3 years exposure. The diffusion coefficients of Metakaolin concrete under both zones are not so much affected by the proportion of binders, and are about 1/5-1/3 times larger than those of OPC and similar to BB. Figure 8 also shows the estimated surface chloride ion content of the all types of concrete. Surface chloride contents of all concretes exposed in the submersed zone are almost the same or slightly higher compared to the ones in the tidal zone. Metakaolin concretes have lower surface chloride content compared to BB. Especially, In the concretes with the binder types of C20:B40:M40 and C20:B60:M20, the surface chloride content is clearly lower comparing to other concretes.

(5) Rebar corrosion

Figure 9 and Figure 10 show the corrosion area ratio of rebars with 2 or 3cm of cover thicknesses in concretes exposed in Tidal zone and submersed zone, respectively. After 1 year exposure in Tidal zone, rebars with 2cm cover thickness in OPC concrete and, Metakaolin concretes with C20:B60:M20 and C20:B40:M40 are observed to have corrosion area of about 1 to 5%. After 3 years of exposure, in these concretes mentioned above, not only the rebars at 2cm cover thickness but also the ones at 3 cm cover are corroded. On the other hand, rebars at 2cm cover thickness of BB concrete and Metakaolin one with C40:B40:M20 type have only corrosion area of less than 1%.



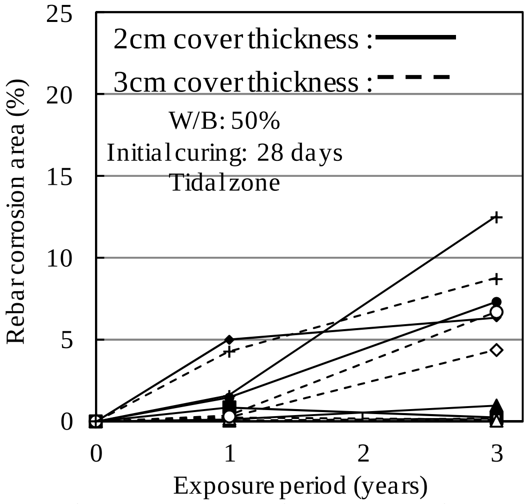


Figure 9. Corrosion area ratio under Tidal zone

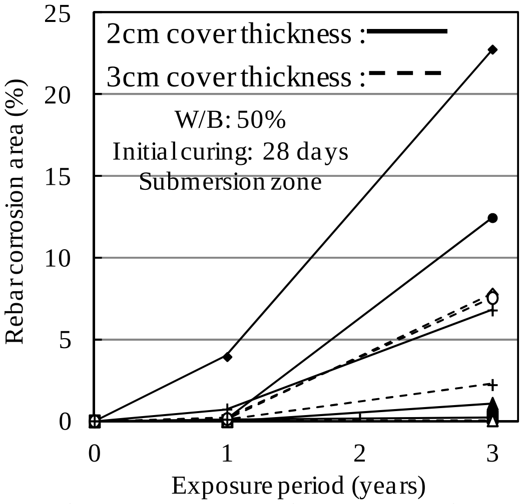


Figure 10. Corrosion area ratio under Submersion zone

In the submersed zone, rebars in OPC concrete and Metakaolin ones with the binder types of C20:B60:M20 and C20:B40:M40 have larger corrosion area than in other concretes, not only after 3 years but also even after 1 year exposure.

These results shows that optimum binder mix proportion in Metakaolin concrete which has similar performance to BB concrete in marione environment can be obtained as C40:B40:M20.

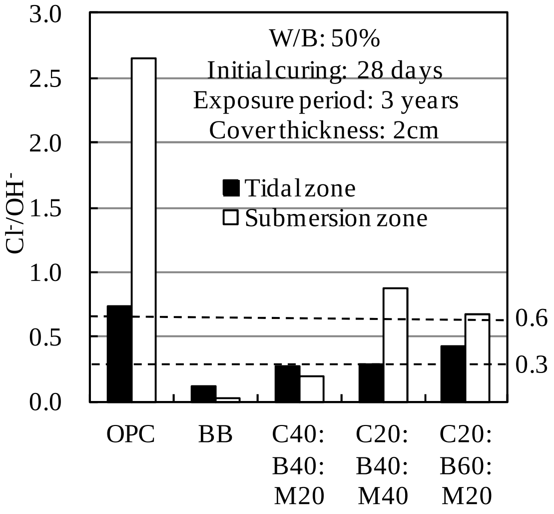


Figure 11. Ratio of free chloride ion to hydroxide ion

From the results of total chloride ion content and the corrosion area ratio of rebars in concrete, it was found that the resistivity of Metakaolin concrete against chloride induced deterioration is not constant and depends on its mix proportion in binders. The results showed that rebars in some Metakaolin concrete corroded even though the total chloride content was almost nil. For clarifying this reason, [Cl^-/OH^-] value in the pores of all types of concrete were examined by the following way. Namely, firstly, soluble chloride content is measured from concretes exposed to marine environment. Secondly, porosity of concrete is measured by mercury intrusion porosimetry at rebar position of specimens. Free chloride content in pore [Cl^-] can be estimated from soluble chlorides content by a correction method (Ishida, 2004). [OH^-] in the pore is also calculated from pH values of each concrete at rebar position. Therefore, the [Cl^-/OH^-] at rebar position are calculated.

Past researches indicate that the threshold value of [Cl^-/OH^-] for initiation of rebar corrosion in concrete should be in the range of 0.3 to 0.6. Figure 11 shows [Cl^-/OH^-] at rebar position of 2cm cover thickness in the all concretes under tidal zone and submersed zone. From the results, it was confirmed that at rebar position in OPC concrete and Metakaolin ones with the binder types of C20:B40:M40 and C20:B60:M20 have higher [Cl^-/OH^-] value than 0.3. This result matches well with the result of corrosion area of rebar in these concretes. Also, at rebar position of Metakaolin concrete of C40:B40:M20 type and BB one, the value is lower than 0.3, hence only slight corrosion area is confirmed. From these result, it is possible to infer the beginning period of corrosion by calculating the [Cl^-/OH^-] even when using Metakaolin. In the concrete using Metakaolin, [OH^-] concentration is apt to reduce because of the shortage of $Ca(OH)_2$ due to the reduction of cement amount and consumption in pozzolanic reaction of Metakaolin. Therefore, even in a case of slight penetration of chloride, it is possible to make the value of [Cl^-/OH^-] higher than threshold value and to initiate the corrosion of rebar in concrete. From the experiment, in the Metakaolin concretes of which cement content is less or equal comparing to the one of Metakaolin, the rebars clearly show corrosion occurrence. For expecting anti corrosion effect under marine environment, it may be necessary to set Metakaolin content in concrete less than 1/2 of that of cement content in the total mix proportion.

4. CONCLUSION

In this study, concrete made with Metakaolin, which is made from industrial by-product is investigated for mechanical properties and durability for long term exposure in marine environment and following conclusions are obtained based on the results:

(1) Resistance against carbonation is low in case of Metakaolin concrete compared to OPC and BB. However, by selecting optimum mix proportion for Metakaolin concrete, carbonation depth reduced to less than 1mm in depth, even when exposed to the marine environment for 3 years.

(2) Partially replacing ordinary Portland cement or ground granulated blast furnace slag one with Metakaolin has the effect of further improving the chloride penetration resistance of concrete.

(3) Anti corrosion effect can be expected by selection of optimum mix proportion for Metakaolin concrete. In this study, good results for strength and durability are obtained for Metakaolin concrete with the binder types of C40:B40:M20.

(4) For evaluating corrosion protection effect on rebar in Metakaolin concrete, not only the reduction of chloride concentration at the rebar portion in concrete, but also the reduction of [OH^-] in the same portion must be considered to estimate the corrosion index [Cl^-/OH^-] more accurately.

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