

# **COMPRESSIVE STRENGTH AND CHLORIDE ION PERMEATION RESISTANCE OF MORTAR CONTAINING CLINKER WITH DIFFERENT MINERAL COMPOSITION AS AN AGGREGATE**

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## **Abstract**

The purpose of this study is to clarify the performance of cement hardenings containing clinkers which are utilized as aggregate by evaluating the compressive strength and chloride ion penetration resistance of the mortars. Here, the fine aggregate used in this study were the ordinary portland cement clinker and the clinker with more waste as an alternative raw material. In addition to this, we discussed on the effect of the clinkers on the compressive strength and chloride ion penetration resistance of mortar based on the weight loss on ignition and void structure. The results showed that the compressive strength of the mortars containing clinker aggregate was equal to or more than the mortar used an ISO standard sand, and the apparent diffusion coefficient of chloride ion decreased by using clinker. The reason why improving compressive strength and chloride ion penetration resistance might be attributed to the densification of the voids in the range of 50 nm to 2  $\mu\text{m}$ , which is considered to be the void diameter represented by the interfacial transition zone, by hydration of clinker itself.

Keywords: cement clinker aggregate, compressive strength, chloride ion permeation resistance

## **1. Introduction**

In Japan, the shortage of final disposal sites has been aggravated in recent years due to the discharge of large amounts of waste. The cement industry is playing an important role as a venous industry by utilizing waste as an alternative raw material for cement clinker and contributes to recycling waste. However, it is extremely difficult to increase the amount of waste utilized for producing cement more than the amount currently utilized because the quality of cement should be controlled at a certain level. In addition to this, the cement production tends to decrease in Japan. Therefore, it is necessary to explore other applications of cement clinker such as aggregate in order to ensure the future capacity of dealing with waste and recycle it. Here, it is becoming more difficult to obtain quality concrete aggregates such as natural gravel and natural sand such as river gravel and sea sand or crushed stone and crushed sand produced by crushing hard rock from the viewpoint of environmental protection and natural resource

protection. Therefore, applying cement clinker as a concrete aggregate has a possibility to contribute to environment preservation and the construction of a sustainable society.

Until now, there are many studies evaluating the performance of cement hardenings improved by using cement clinker aggregate and considering the mechanism of it. Previous studies reported that applying cement clinker as fine aggregate encouraged to produce hydrate formation and densify in the interfacial transition zone between aggregate and cement paste by hydration of cement clinker itself [1][2]. Here, in consideration of the relationship between mass transfer in cement hardening and void structure including interfacial transition zone [3], mass transfer resistance can be expected to improve by using cement clinker. In addition, they also reported that compressive strength of cement hardenings containing clinker as an aggregate became higher than that of cement hardenings containing an ISO standard sand because interfacial transition zone densified by using cement clinker aggregate. In this way, using cement clinker as an aggregate instead of ISO standard sand enable to improve compressive strength and mass transfer resistance.

On the other hand, the cement industry in Japan can produce various types of clinkers to accept more industrial waste and industrial by-products. The typical example is the eco cement clinker which is produced from a large amount of waste such as incineration ash of city garbage that is difficult to treat. Similarly, belite gehlenite clinker is also a promising one because it can treat industrial waste more than ordinary portland cement clinker. From the above, it can be pointed out that applying cement clinker aggregate can contribute to constructing a sustainable society by producing more durable concrete and environment preservation. Here, there are few studies on cement hardenings containing clinker aggregates at the long-term age, and studies on cement hardenings containing eco cement clinker aggregate and belite gehlenite clinker aggregate. Consequently, in regard to cement hardenings containing various clinker aggregates, it is necessary to examine in the long term that there is no problem in strength and durability or whether it contributes to improvement of these performances. Therefore, the purpose of this study is to evaluate the basic physical properties and mass transfer resistance of the mortars with the clinker fine aggregates. In addition to this, we discussed on the effect of the clinker aggregates on the compressive strength and the apparent diffusion coefficient of chloride ion of the mortars based on the loss of ignition and void structure.

## **2. EXPERIMENTAL PROCEDURES**

### **2.1 Materials**

In this study, the ordinary portland cement conforming to JIS R 5201: 2015 and JCAS K-03 was used as a binder. The fine aggregates were an ISO standard sand defined according to JIS R 5201 (hereinafter called “SS”), an ordinary portland cement clinker (hereinafter called “NCL”), an eco cement clinker (hereinafter called “ECL”), and two types of belite gehlenite clinker with different mineral compositions (hereinafter called “V1CL and V2CL”) for the purpose of evaluating the effect of clinker types on compressive strength and chloride ion penetration resistance of the mortars. Table 1 shows the density in oven-dry condition, the water absorption and the mineral composition of various clinkers. These clinkers as fine aggregates had the same particle size distribution as SS by crushing and sieve classification.

**Table 1 : Absolute dry density, water absorption and mineral composition of the fine aggregates**

| Clinker | Absolute Dry Density (g/cm <sup>3</sup> ) | Water Absorption (%) | Content Ratio (%) |                  |                   |                  |                   |       |
|---------|---|----------------------|-------------------|------------------|-------------------|------------------|-------------------|-------|
|         |   |                      | C <sub>3</sub> S  | C <sub>2</sub> S | C <sub>2</sub> AS | C <sub>3</sub> A | C <sub>4</sub> AF | f.CaO |
| NCL     | 2.66                                      | 4.20                 | 54.2              | 25.2             | 0.0               | 9.2              | 11.2              | 0.0   |
| ECL     | 2.78                                      | 3.39                 | 55.6              | 16.5             | 0.0               | 11.8             | 15.0              | 0.3   |
| V1CL    | 2.94                                      | 2.38                 | 0.0               | 75.7             | 19.2              | 0.0              | 5.1               | 0.0   |
| V2CL    | 2.88                                      | 1.35                 | 0.0               | 47.7             | 52.1              | 0.0              | 0.1               | 0.0   |

## 2.2 Sample Preparation

The water cement ratio (hereinafter called “W/C”) was held at 50 percent and the fine aggregates cement ratio (hereinafter called “S/C”) was held at 2.5 at all levels. Table 2 shows the mix proportions of the mortars. The mortars were mixed in accordance with JIS R 5201. The fresh mortar was mixed until the bleeding was settled, and was put into a plastic disposable mold with an internal dimension of  $\phi 50 \times 100$  mm. After  $24 \pm 2$  hours, the mold was removed, and hardened mortar was performed water curing for up to 91 days in a saturated aqueous solution of calcium hydroxide. However, the samples for the measurement in 1 day of the material age were tested immediately after demolding. Besides, the mortars containing SS, NCL, ECL, V1CL and V2CL as fine aggregates are referred to as SS-M, NCL-M, ECL-M, V1CL-M and V2CL-M respectively.

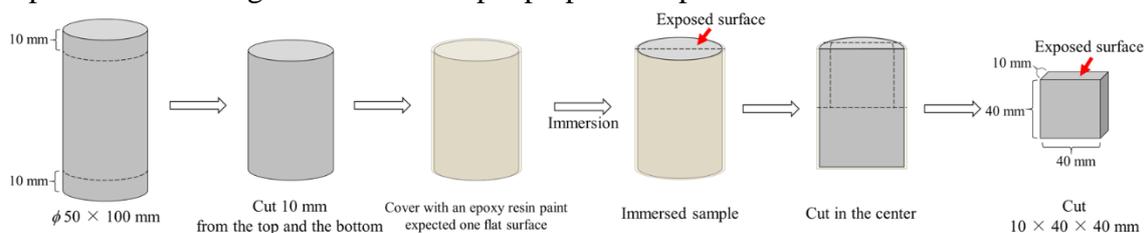
**Table 2: Mix proportion of mortar made with SS and cement clinker aggregates**

|        | Water/Cement (-) | aggregate/Cement (-) | Water (kg/m <sup>3</sup> ) | Cement (kg/m <sup>3</sup> ) | Aggregate (kg/m <sup>3</sup> ) |
|--------|------------------|----------------------|----------------------------|-----------------------------|--------------------------------|
| SS-M   | 0.5              | 2.5                  | 284                        | 567                         | 1418                           |
| NCL-M  |                  |                      | 285                        | 569                         | 1423                           |
| ECL-M  |                  |                      | 291                        | 583                         | 1457                           |
| V1CL-M |                  |                      | 300                        | 600                         | 1500                           |
| V2CL-M |                  |                      | 297                        | 594                         | 1484                           |

## 2.3 Testing Procedure

Using the samples in up to 91 days, the measurement of ignition loss (measurement range: 105 °C) by thermogravimetry differential thermal analysis (hereinafter called “TG-DTA”), the measurement of total porosity and pore size distribution by mercury intrusion porosimetry (hereinafter called “MIP”), the observation of aggregate interface by scanning electron microscope (hereinafter called “SEM”), the compressive strength test and the salt water immersion test were carried out. In addition, ignition loss is the total amount of bound water and calcium carbonate. The compressive strength test was performed 3 times per each case and the average of the three measurement results was defined as the testing result. The immersion test was carried out as the following. The mortar sample of  $\phi 50 \times 100$  mm at a material age of 28 days was cut 10 mm from the top and the bottom. The cut sample was covered with an epoxy resin paint excepted one flat surface. The covered sample was immersed in 3 percent NaCl solution for 28 days so that the solid-liquid ratio was 1 : 20. After that, the measurement sample for chloride ion concentration distribution in the mortar was obtained by cutting the immersed

sample so that the measurement sample dimension was  $40 \times 40 \times 10$  mm and the sample has the exposed surface. Figure 1 shows sample preparation procedure.



**Figure 1: Sample preparation procedure**

The surface analysis of the chloride ion concentration distribution in the sample was performed by an electron probe microanalyzer (hereinafter called “EPMA”). After that, the apparent diffusion coefficient of chloride ion was calculated by applying the concentration distribution of chloride ion obtained from EPMA to diffusion equation based on Fick’s law shown in Eq.(1) and regression analysis of the total chloride ion concentration by each depth of the sample:

$$C(x,t) - C_i = C_{a0} \left\{ 1 - \operatorname{erf} \left( \frac{x}{2\sqrt{D_{ap} \cdot t}} \right) \right\} \quad (1)$$

where  $t$  is immersing period,  $C(x,t)$  is total chloride ion concentration of mortar per unit volume at  $x$  meter deep in  $t$  year,  $C_{a0}$  is total chloride ion concentration of mortar per unit volume on the surface by the immersion test,  $C_i$  is total chloride ion concentration of mortar per unit volume contained originally,  $D_{ap}$  is apparent diffusion coefficient.

### 3. RESULT AND DISCUSSION

#### 3.1 Effect each clinker aggregate on compressive strength

Figure 2 shows the relationship between the porosity of voids in the range of 50 nm to 2  $\mu$ m and the ignition loss, Figure 3 shows the compressive strength in each day and Figure 4 shows the relationship between the increasing rate of compressive strength to the material age of 1 day and the decreasing rate of the porosity of voids in the range of 50 nm to 2  $\mu$ m to the material age of 1 day. Here, these rates were calculated from the following Eq. (2) and Eq. (3):

$$\Delta F_n = \frac{F_{nd} - F_{1d}}{F_{1d}} \times 100 \quad (n = 7, 28, 56) \quad (2)$$

$$\Delta P_n = \frac{P_{nd} - P_{1d}}{P_{1d}} \times 100 \quad (n = 7, 28, 56) \quad (3)$$

where  $\Delta F_n$  is the increasing rate of compressive strength to the material age of 1 day,  $F_{1d}$  is compressive strength at the material age of 1 day,  $F_{nd}$  is compressive strength at the material age of  $n$  days,  $\Delta P_n$  is the decreasing rate of the porosity of voids in the range of 50 nm to 2  $\mu$ m to the material age of 1 day,  $P_{1d}$  is the porosity of voids in the range of 50 nm to 2  $\mu$ m at the material age of 1 day and  $P_{nd}$  is the porosity of voids in the range of 50 nm to 2  $\mu$ m, which is the void constituting the tranzisiton zone, at the material age of  $n$  days.

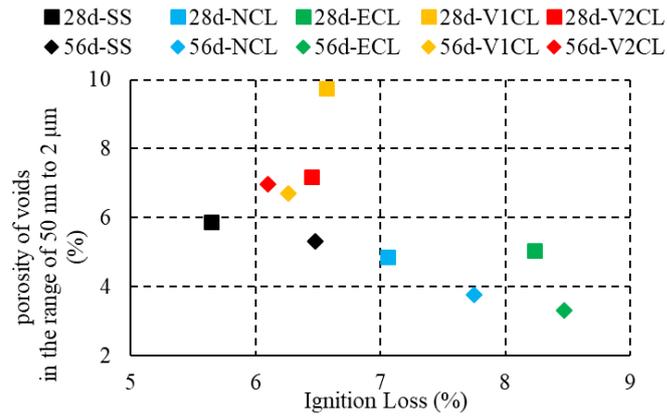


Figure 2: the relationship between the porosity of voids in the range of 50 nm to 2 μm and the ignition loss

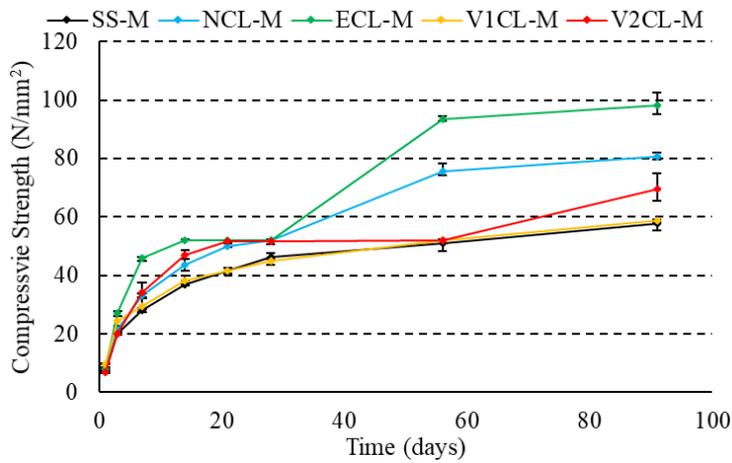


Figure 3: the compressive strength in each days

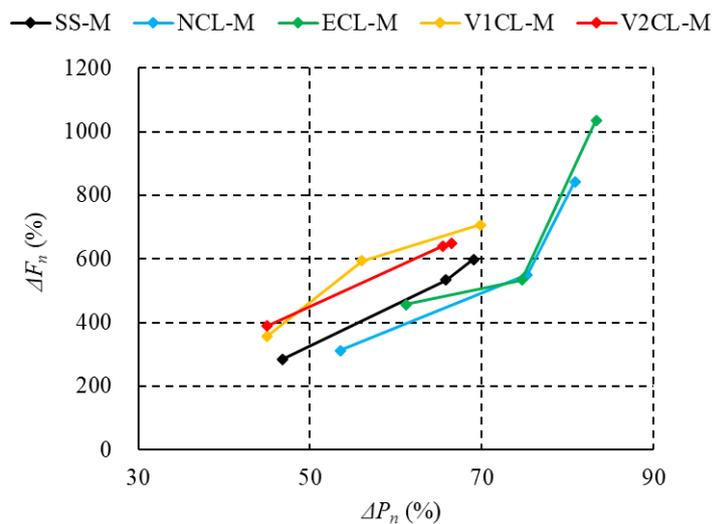


Figure 4: the relationship between  $\Delta F_n$  and  $\Delta P_n$

Figure 2 is a graph focusing on the relationship between the porosity of the voids in the range of 50 nm to 2  $\mu\text{m}$ , and ignition loss in order to investigate the change in the content of hydrate affect porosity. As shown in Figure 2, in regard to SS-M, NCL-M and ECL-M, the porosity decreased with increasing ignition loss. In contrast, V1CL-M and V2CL-M didn't show this tendency. However, in regard to V1CL-M, ignition loss at a material age of 28 days was 7.4 percent and increased from a material age of 28 days to that of 91 days. Considering these results, it was suggested the possibility that the increase in ignition loss has contributed to the decrease in porosity of voids in the range of 50 nm to 2  $\mu\text{m}$ . Besides, NCL-M and ECL-M had more ignition loss and fewer voids in this range than SS-M. As a reason for this, it is mentioned that since NCL and ECL contain a relatively large amount of alite and aluminate phase, which have high hydration activity, the transition zones around NCL-M and ECL-M were densified by themselves hydration reaction [4]. In contrast, it was inferred that V1CL and V2CL contain belite and gehlenite as the main mineral, which has low hydration activity, the porosity of this range of V1CL-M and V2CL is not as small as SS-M.

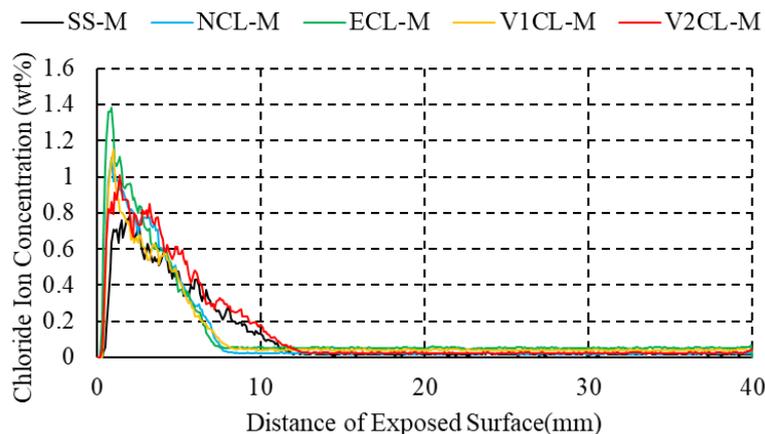
Figure 3 shows the change with time in compressive strength. As shown in Figure 3 in regard to the material age of 91 days, the mortars containing clinker fine aggregates showed equal or higher compressive strength than SS-M. NCL-M and ECL-M in particular, showed higher compressive strength than SS-M.

Figure 4 shows the relationship between  $\Delta F_n$  and  $\Delta P_n$ . As shown in Figure 4, all cases showed that the more decreasing rate of the porosity of voids in this range, more the rate of increase in compressive strength. As mentioned above, the void in this range is regarded as the transition zone, and it is reported that the smaller the void in this range, the higher the compressive strength [3]. Therefore, in this study, it is possible that the densification of the transition zone has contributed to increasing the increasing rate in compressive strength. It was suggested that NCL-M and ECL-M had more increasing rate of compressive strength than SS-M, because they particularly had the more decreasing rate of the porosity of the void in this range.

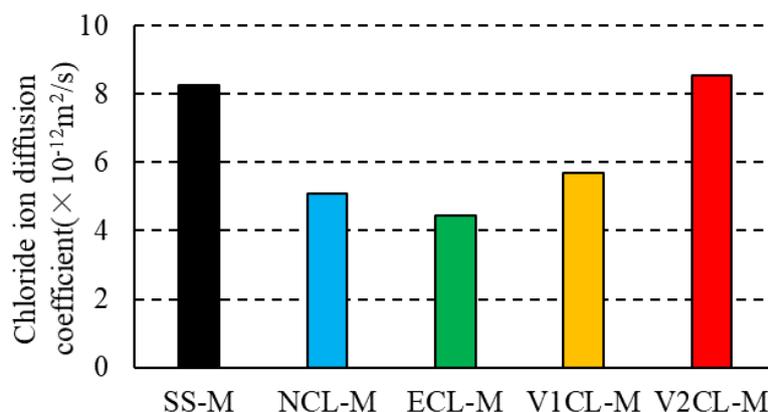
From the above, it was suggested the possibility that the compressive strength of mortars containing V1CL and V2CL, which is considered to have low hydration activity, was comparable to that of mortar containing SS. Similarly, it was also suggested the possibility that the compressive strength of mortars containing NCL and ECL, which is considered to have high hydration activity, were high than that of mortar containing SS.

### 3.2 Effect each clinker aggregate on the apparent diffusion coefficient of chloride ion

Figure 5 shows the concentration distribution of chloride ion in mortar immersed for 28 days and Figure 6 shows the apparent diffusion coefficient of chloride ion. As shown in Figure 5, in regard to chloride ion penetration depth, V2CL-M was comparable to SS-M, and NCL-M, ECL-M and V1CL-M were lower than SS-M. Therefore, the apparent diffusion coefficient of chloride ion at each case was calculated and shown in Figure 6. As shown in Figure 6, focusing on the relationship between the difference in fine aggregate and the apparent diffusion coefficient of chloride ion, the apparent diffusion coefficient of chloride ion was smaller in the order of ECL-M, NCL-M, and V1CL-M, and these of SS-M and V2CL-M were almost the same. Considering this point, chloride ions move through the voids in the cement hardening, and gaps in the transition zone have a significant effect on mass transfer [5]. Therefore, it is suggested that the densification of the transition zone contributed to suppressing chloride shift with clinker, which is considered to have high hydration activity.

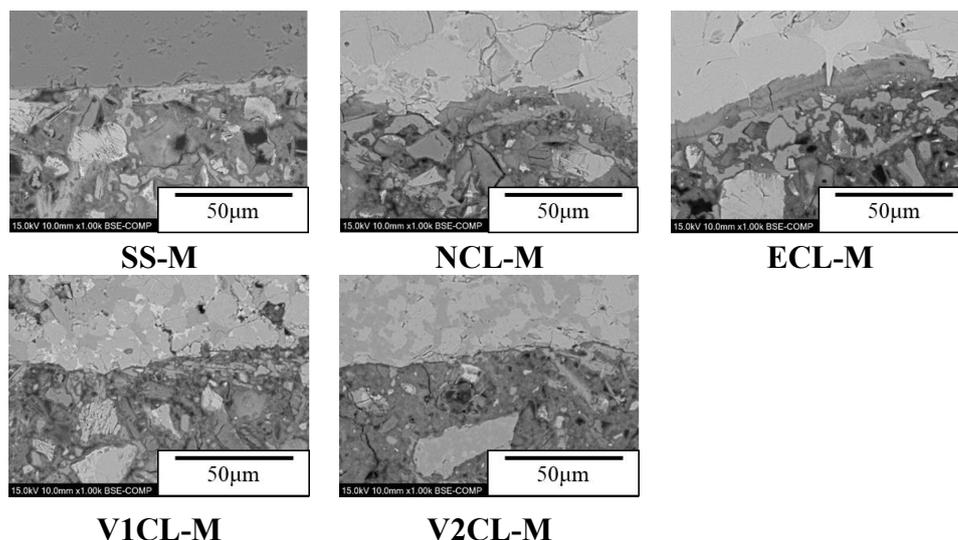


**Figure 5: the concentration distribution of chloride ion in mortar immersed for 28 days**



**Figure 6: the apparent diffusion coefficient of chloride ion**

It was previously inferred that the transition zone was densified from the relationship with ignition loss, porosity and compressive strength with clinker, which is considered to have high hydration activity. By contrast, here, chloride ion penetration resistance was evaluated by acquiring a backscattered electron image with SEM and observing the condition around the transition zone for each aggregate. Figure 6 shows the backscattered electron images. As shown in Figure 7, in regard to NCL-M and ECL-M, there was no gaps around the transition zone and precipitate such as hydrate were observed. In contrast, in regard to SS-M, V1CL and V2CL-M, there were gaps with different width. Similarly, from this result, it was suggested the possibility that the densification of the transition zone caused by precipitation of hydrate contributes to the improvement of chloride ion penetration resistance with clinker, which is considered to have high hydration activity.



**Figure 7: the backscattered electron images**

#### 4. Conclusions

In this study, focusing on the basic physical properties and mass transfer resistance of mortars containing clinkers which are utilized as aggregate, the effects on these properties were evaluated. These results showed that mortar containing clinker fine aggregate performed equal or higher compressive strength and equal or lower apparent diffusion coefficient of chloride ion than SS-M. Besides, the results obtained from the compressive strength test showed the tendency to improve compressive strength in the long term. It was suggested that the main reason that the clinker fine aggregates contributed to the improvement in compressive strength and chloride ion penetration resistance was the densification of the transition zone by the hydration reaction of clinker, which is considered to have high hydration activity.

#### References

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