Microstructures of Hardened Mortars Using Eco-Cements and Sintered Sewage Sludge

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エコセメントと溶融下水汚泥を使用したモルタル硬化体の微細構造

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Strength development and microstructures were investigated for a hardened mortar using eco-cement manufactured by replacing a part of the raw materials with incineration ash of urban waste and a waste-derived aggregate of sintered sewage sludge. Back-scattered electron images and X-ray image maps showed that the porous zones of $Ca(OH)_2$ usually observed at the interface between the normal Portland cement paste and aggregate did not form in mortars using the eco-cements. The hydration processes of eco-cements were discussed based on distribution maps of Cl, S, Mg, Na, K, Fe, Si, Al, Ca, and O.

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1. Introduction

Discharges of incineration ash of urban refuses and industrial wastes have been increasing every year, and shortage of disposal centers has become a vital problem in environmental conservation. During recent years, substantial efforts have been made in reducing and recycling these wastes. In order to utilize such waste materials and at the same time to preserve natural resources, techniques to manufacture cements from the incineration ash of urban refuses and sewage sludge have been developed.^{1),2)} These cements were called eco-cements after their environmental load-reducing properties. Because of the difference in the raw materials, their mineralogical compositions and hydration behavior differ from the normal Portland cement (NPC). However, the microstructures of hardened mortar and concrete using eco-cements have not been clarified so far

The strength, gas and water permeability, ion penetrability, and durability of concrete are associated with the pore structure, orientation, and crystal habit of $Ca(OH)_2$ generated at the transition zone formed at the interface between the cement paste and the aggregate. As for the ordinary concrete from NPC and natural aggregates, the texture and the composition of the transition zone have been elucidated, and the techniques for the control of the hardened concrete structure have been established.³⁾⁻⁵⁾ However, there are no reports on the interface structures of the eco-cements between the cement paste and the aggregates. In order to verify the durability and the usefulness of the eco-cements, it is necessary to elucidate their microstructures.

Furthermore, high-volume recycled waste concrete (HVRWC) containing several hundred kilograms or more of waste derived materials as aggregates per cubic meter of concrete using NPC has been proposed.⁶⁾ The structure and the strength of the hardened HVRWC have been reported for various kinds and amounts of waste-derived aggregates such as incineration ash of urban refuse, sintered coal ash, sintered sewage sludge, and glass cullet.⁷⁾ In view of environmental conservation, it is highly desirable to prepare HVRWC from both the eco-cement and the waste-derived aggregate. The study of interfacial structures between the

eco-cement and the waste-derived aggregates will provide great information on the utility of HVRWC.

In this paper we focused on the microstructures of hardened mortars prepared from eco-cements, especially on the interfacial zone structure between the cement paste and the aggregate observed by means of scanning electron microscopy (SEM) and electron probe microanalysis (EPMA):

2. Experimental

2.1 Sample preparation Mortar specimens (160 mm × 40 mm × 40 mm) were prepared using three types of cement: normal Portland cement (NPC), normal-type eco-cement with low chlorine (NEC), and rapid-hardening type eco-cement with high chlorine (REC), and two types of fine aggregates: Japanese Industrial Standard (JIS) natural sand and water-quenched sintered sewage sludge (SS). Their chemical composition, mineralogical composition and surface area properties are shown in Table 1. The mineralogical compositions of the REC was estimated by using the following equations based on the assumption that the compositions of the four major phases are C_3S , C_2S , $C_{11}A_7$. CaCl₂, and C_4AF .

$$\label{eq:G3S} \begin{split} &\% C_3 S = 4.071 CaO - 2.852 SO_3 - 7.602 SiO_2 \\ &- 5.718 Fe_2 O_3 - 3.519 Al_2 O_3 \\ &- 3.220 Cl + 3.683 Na_2 O + 2.424 K_2 O \quad (2.1) \\ &\% C_2 S = 2.867 SiO_2 - 0.7544 C_3 S \quad (2.2) \\ &\% C_{11} A_7 \cdot Ca Cl_2 = 2.020 Al_2 O_3 - 1.290 Fe_2 O_3 \quad (2.3) \end{split}$$

$$%C_4AF = 3.043Fe_2O_3$$
 (2.4)

In Eq. 2.1, the terms of Na₂O and K₂O were added by assuming that Na₂O and K₂O react with calcium compound to liberate CaO. On the other hand, the reaction of MgO was not taken into account because most of it distributed independently as MgO during hydration, as discussed in Results and discussion section. The mixing ratio of mortar of cement : aggregate : water: was 1:3:0.5, and the specimens were cured in water at 20°C according to JIS R 5201.

2.2 Characterization

Bending strength and compressive strength tests of the

		Binder			Fine Aggregate	
		NPC	NEC	REC	SS	Sand
Blaine Specific Surface Area / cm ² g ⁻¹		3470	4500	5710		
	SiO ₂	20.7	17.5	15.7	41.6	98.4
	Al ₂ O ₃	4.8	8.1	9.4	13.0	0.4
	Fe ₂ O ₃	2.9	3.9	2.2	10.0	0.4
	CaO	64.8	61.1	58.7	16.9	0.2
Chemical	MgO	1.1	1.9	2.0	2.2	
Compostion	SO ₃	2.0	3.7	8.5		
/ %	Na ₂ O	0.4	0.2	0.4	1.3	0.01
	K ₂ O	0.4	0.02	0.05	2.6	0.01
	Cl	0.008	0.07	0.9		
	TiO ₂	0.3	0.6	0.6		
	P ₂ O ₅	0.2	1.2	1.0	10.0	
	Total	99.8	98.3	99.5	97.6	till and a state of the second se
	C ₃ S	51.9	45.3	48.4		
Mineralogical	C_2S	20.2	16.0	8.5		
Compostion	Ċ ₃ A	7.8	14.9	-		
1%	C ₁₁ A ₇ ·CaCl ₂	-	-	16.2		
an tha an tao	C ₄ AF	8.8	11.9	6.7		

Table 1.Chemical and Mineralogical Compositions of the Cements and the AggregatesNPC, Normal Portland Cement; NEC, Normal-Type Ecocement; REC, Rapid-Hardening Type Ecocement; SS, Sintered Sewage Sludge

mortar specimens were carried out at the ages of 3, 7, 14, and 28 d. SEM and EPMA (JXA-8800, JEOL) observations and analysis were carried out on specimens at the age of 28 d. The specimens were dry-polished and characterized at the acceleration voltage of 15 kV and the irradiation current of 0.1 μ A.

3. Results and discussion

3.1 Mechanical strength

Figures 1 (a) and (b) show the compressive and bending strengths of the mortar specimens, respectively. As for the compressive strength, the eco-cements showed very similar strengths as the NPC at the age of 28 d though the early strengths of REC are higher than those of NPC and NEC, when the standard sand was used as aggregate. On the contrary, when the SS was used, the two types of eco-cements showed slightly higher strengths than the NPC. The result suggests that the combination of the eco-cements and SS is comparable to that of NPC and sand after 28 d.

As for the bending strength, the specimens using the SS were inclined to show lower strength, by about 10–20 percent, than those using the standard sand. This difference can be ascribed to lower adhesive strength between the aggregate and the cement paste due to the glassy smooth surface of SS rather than to the strength of the aggregate itself. The REC and the NEC using the SS showed higher strengths than in the case of NPC using the SS. The influence of the surface smoothness of the SS on the bending strengths was smaller in the case of eco-cements than in the case of the NPC.

3.2 Microstructure

The observed changes in strength are closely related with the microstructure of mortar, especially with the interfacial microstructure between the cement paste and the

aggregate.⁴⁾ Figure 2(a) shows a back-scattered electron image on the polished surface of hardened mortar using NEC and standard sand. The white parts of the image corresponds to unhydrated calcium silicates since the X-ray image maps in Fig. 3(a) showed high contents of calcium and silicon at the part. The distribution of sodium coincides with that of the unhydrates, indicating that most of the sodium still exists in unhydrated solid solution. The distribution of magnesium does not necessarily correspond to those of the unhydrated calcium silicate or the chlorine, and part of the magnesium distribution correspond to that of iron. This indicates that the magnesium did not exist as a solid solution of calcium silicate such as $C_{54}S_{16}AM^{(8)}$ nor form chloride during hydration, and that most of the magnesium exists as periclase (MgO), brucite $(Mg(OH)_2)$ and the solid solution of C_4AF . It is exciting to note that the porous calcium-rich phase mainly consisting of Ca(OH)₂ usually observed around the aggregate in the NPC mortars of water: cement ratio of 0.4 or more^{4),5)} was not observed in the present ones having a water to cement ratio of 0.5. This indicates that the transition zone is not formed at the conventional water: cement ratio in the mortar using the NEC. Thermogravimetry and powder XRD measurement also indicated that the calcium hydroxide did not form in the specimen at the age of 28 d, and the formation of the ettringite was observed in the XRD profiles. These can mainly be ascribed to the lower content of C₃S and C₂S in the eco-cement, and the calcium hydroxide formed by the hydration of NEC is assumed to be easily consumed to form ettringite.

Figures 2(b) and 3(b) show a back-scattered electron image and an X-ray image map of mortar using the REC and the standard sand, respectively. The transition zone was not observed in Figs. 2(b) and 3(b) similarly to the case with the NEC and the standard sand. These results indicate the





Fig. 1. Compressive strength (a) and bending strength (b) of the mortar specimens using three types of cements and two types of fine aggregates. NPC, normal Portland cement; NEC, normal type eco-cement; REC, rapid-hardening type, eco-cement; SS, sintered sewage sludge.

adhesion between the two types of eco-cement paste and the sand were satisfactory, and this corresponds to the fact that their 28 d strengths were comparable to those of the NPC. The REC contains 0.9% of chlorine and 8.5% of SO₃ as shown in Table 1, and this can be also confirmed by the image map. The white parts of the image, which contain high content of calcium and silicon and hardly contain chlorine, corresponded to unhydrated calcium silicates in a similar manner as in the case of NEC (Figs. 2(a) and Fig. 3(a)). It is confirmed by these distributions that little alinite (C_3S) . $CaCl_2$) or $C_2S \cdot CaCl_2$ are formed in the eco-cements.⁹⁾ The size of the unhydrated calcium silicate is smaller because the hydration proceeds much more due to its higher hydration activity than calcium silicate phase in NEC and NPC. It is not clear so far whether this difference in hydration activity is caused by the difference in mineralogical compositions and crystal structures such as distortion, or in specific area. The distribution of chlorine almost corresponds to those of sulfur and aluminum. The concentrations of chlorine, sulfur, aluminum, and calcium in the chlorine-concentrated region are estimated as 1.5, 5, 9 and 30%, respectively. This provides significant information on hydration products. Chemical compositions of aluminum and sulfur in ettringite $(3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O)$ are 4.3 and 7.7%, and those in monosulfate hydrate $(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O)$ are



Fig. 2. Back scattered electron images on the polished surface of the mortars from (a) NEC and sand, (b) REC and sand, (c) NEC and sintered sewage sludge, and (d) REC and sintered sewage sludge.



After mixing with water, ettringite is formed by hydration of calcium chloroaluminate $C_{11}A_7 \cdot CaCl_2$ with gypsum, and it converts into monosulfate hydrate with time. In the process of hydration, about 10% or more of the monosulfate hydrate reacts with Cl⁻ liberated from $C_{11}A_7 \cdot CaCl_2$ to form Friedel's salt.

Figures 2(c) and (d) show back scattered electron images of hardened mortars using the SS as aggregate with NEC and REC, respectively. The surface of the SS was found to be smooth compared with that of the sand, and the



Fig. 3. X-ray image maps of mortars from (a) NEC and sand, (b) REC and sand, (c) NEC and sintered sewage sludge, and (d) REC and sintered sewage sludge.

transition zones were not observed also for these mortars. The surface smoothness of SS is due to the deposit of glass phase in the treatment process of sintering and waterquenching.¹⁰ Although the absence of the transition zone is favorable to strength, the surface smoothness of the aggregates can cause a reduction of the adhesive strength and consequently the lowering of the strengths, especially the bending. As shown in Figs. 3(c) and (d), the behavior of the cement pastes were almost the same as the cases using the standard sand. The same discussions on the distributions of each element are possible, and this indicates that chemical components affecting the hydration of cement do not elute from the waste-derived aggregate.

4. Conclusions

The strength and the microstructures of hardened mortars using eco-cements and the waste-derived aggregates were investigated. Results obtained are summarized as follows: (1) The strengths of the specimens using the eco-cements were comparable to those of the NPC. The decrease in strengths, particularly bending strengths, of mortars using SS was thought to be due to its glassy smooth surface.

(2) The transition zone usually observed as a porous calcium-rich zone around the aggregate in NPC mortars of water: cement ratio of 0.4 or more was not formed in the eco-cement mortars having a water to cement ratio of 0.5. This is considered to be due to the accelerated consumption of $Ca(OH)_2$ produced by the hydration of eco-cements to form ettringite owing to their lower contents of C_3S and C_2S .

(3) The distribution of magnesium in hardened mortar did not necessarily correspond to those of calcium and silicon, indicating that the most of magnesium existed as periclase (MgO), brucite (Mg(OH)₂) and the solid solution of C₄AF.

(4) The distribution of chlorine indicated that little chlorine did not exist in alinite $(C_3S \cdot CaCl_2)$ or $C_2S \cdot CaCl_2$ are formed in the eco-cements, and that it is incorporated into

Friedel's salt produced by reaction with 10% or more of monosulfate hydrate.

(5) The size of the calcium silicate of the REC which remained unhydrate was smaller than that of the NEC, showing its high reactivity.

(6) Chemical components affecting the hydration of cement are deduced not to be eluted from the waste-derived aggregate.

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