Strength Development and Its Microstructure of Eco-cement Paste

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1. Introduction

The processing problem of the significant amount of incineration ash transported to landfills occurs in the large city such as Tokyo in Japan. Therefore, cement that made the household waste a raw material was manufactured in the cement industry. Eco-cement that is made of municipal waste incineration ash and sewage sludge for at least half of the raw materials was developed and Japanese Industrial Standard (JIS) was enacted in 2002. The concrete structures that made by eco-cement are few although eco-cement was made standard as JIS. There is not so much long-term strength development of concrete that used eco-cement although initial strength development is large [1, 2]. Therefore, use of fly ash, slag or lime stone powder as admixtures has been investigated for increasing the strength at long term [3-8]. However, the research about the mechanism of the strength development is hardly seen now. It is thought that the number of cases that a lot of wastes will be used for cement as a recycling material in the future increase. It is very important to clarify the strength development mechanism of concrete that uses waste for that.
Therefore, it aimed to clarify the mechanism of the strength development of the hardened cement paste that used eco-cement in this study.

2. Experimental

2.1 Sample preparation

Ordinary Portland cement (OPC, 3160kg/m3) and Eco-cement (ECO, 3130kg/m3) were used in this study. Properties of cements and chemical composition of cements is shown in Table1, 2, respectively.
The water to cement ratio of the cement paste is 0.4, 0.5 and 0.6 by weight. Mixing time was 3 minutes. Cement pastes were cast in cylindrical moulds. Each of them was sealed at 20ºC for 1, 3, 7, 28, and 91days. The hydration degree of each paste was determined by using the ignition loss technique (105- 950ºC).

Table 1 Properties of cements

Sample	Blaine (cm^2/g)	Density (g/cm^3)	Ig.loss (%)
OPC	3450	3.16	0.83
EC	4310	3.17	1.02

Table 2 Chemical compositions of cements

	Chemical composition (%)					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
OPC	20.93	5.16	2.97	64.16	2.48	2.11
ECO	18.01	7.42	3.72	61.63	2.24	4.09

2.2 Backscattered Electron Image (BEI) measurement

Specimens of 5 cubic millimeters of pastes were prepared and immersed in acetone for approximately 24 hours to remove most of the water by solvent exchange. D-dry was applied to specimens to remove most of the acetone. They were immersed in low viscosity epoxy resin under vacuum at room temperature. After the impregnated resin was hardened, the surface of specimens was polished with sand paper and then with diamond paste. Finally, carbon was coated. The specimens were examined at 500x at 15 KeV by SEM with BSE detector. Observation area is 150 x 200 μm and each pixel size is 0.32μm. And degree of hydration α_c is determined by following equation,

$$\alpha_c = 1 - \frac{V_{ci}}{V_{c0}} = 1 - \frac{A_{ci}}{A_{c0}}$$

where Vci, Vc0, Aci and Ac0 is volume of cement at time i, volume of cement at initial, area fraction of cement at time i and area fraction of cement at initial respectively.

2.3 Energy Dispersive X-ray analysis (EDX) measurements

The measurement condition of EDX is same as BEI measurement without measuring pixel size. The measuring pixel size is 256x256. In this study, the elements of Na, Mg, Al, Si, P, S, K, Ca and Fe are detected. And threshold value of each element is determined by measuring each phase using point analysis. The decision algorithm of the phase in hardened cement paste is not reported, though Bentz[9]reported on the decision algorithm of distribution of phases in the cement particle. In this study, the algorithm of determination of each phase distribution in hardened cement paste is shown in Fig.1. Firstly, when the pixel in BEI is brighter than that of Aluminate in unhydrated cement particle, the pixel is unhydrated cement. When it is darker than Aluminate, it is pore, $Ca(OH)_2$, CSH or other hydration products. When the pixel of unhydrated cement contains Al and Fe in unhydrated cement, it is Ferrite phase. When the pixel does not contain Fe, it is Aluminate phase. It is Alite phase in case the Ca/Si ratio of the other pixels is high. The rest of pixels in unhydrated cement are Belite phase.

The pixel that does not indicate the value of Ca is pore (≥0.32μm), and the pixel that shows no value of Si and high value of Ca is calcium hydroxide and the other pixels are CSH or other hydration products including fine pores(<0.32μm).

2.4 Compressive strength measurement

The measurement of compressive strength was determined by using cylindrical specimen with a 100mm height and a 50mm diameter.

3. Measurement result and consideration

3.1 Compressive strength measurement result

Fig.1 shows the measurement result of compressive strength. The compressive strength of EC is higher than that of OPC. At 91days, the compressive strength of OPC is higher than that of EC.

3.2 Degree of hydration measurement result by BEI

Fig.2 shows the measurement result of W/C 0.5 of BEI on 1day and 28days. A white portion shows the unhydrated cement particle and a brighter gray shows CH and a dark gray show CSH and the black shows the pore. A lot of pores exist and a lot of unhydrated cements remain in both cements at 1day. The pore and unhydrated cement could hardly be observed though the hydration products were observed at 28days. A lot of needle hydrates thought to be Ettringite or monosulfoaluminate were also observed in eco-cement paste at 28days. This tendency was observed in other W/C. Fig.3 shows the phases in hardened cement paste (w/c:0.6). At 3day the fraction of porosity and unhydrated cement of eco-cement are smaller than those of OPC. On the contrary, those of OPC are smaller than those of EC at 91days.

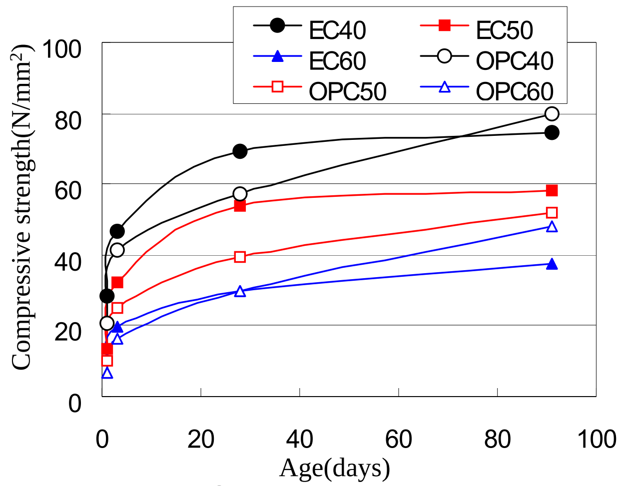

Fig.1 Strength development

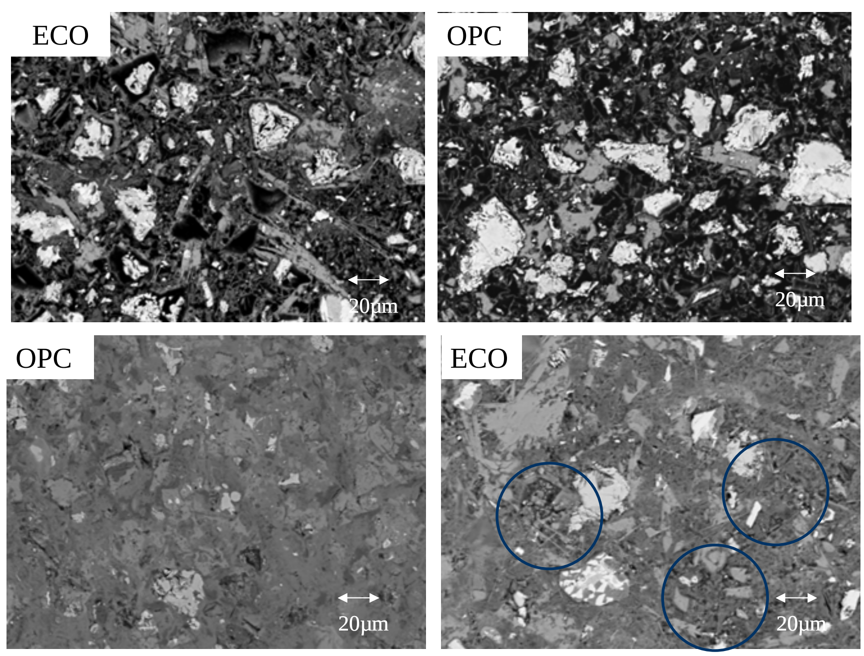

Fig.2 BEI of OPC and ECO cement paste with W/C 0.5
(upper :1day, lower :28day)

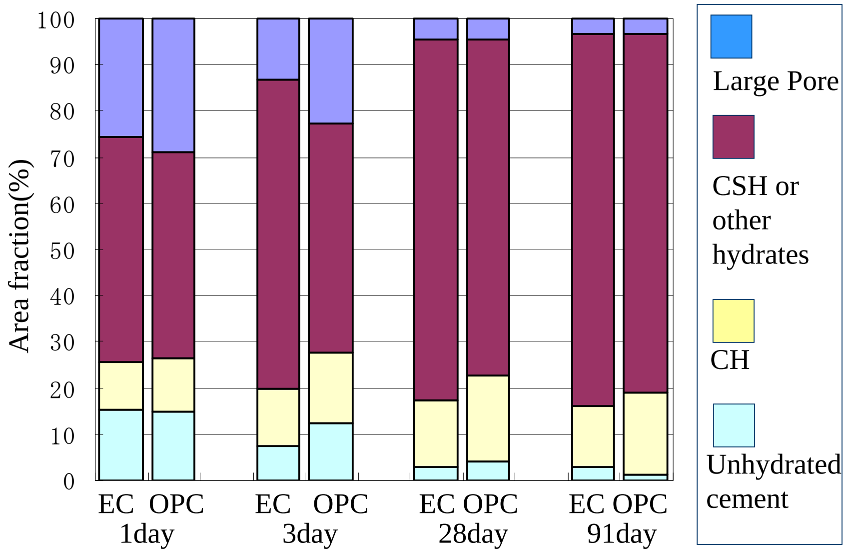

Fig.3 Phases in hardened cement paste (w/c:0.6)

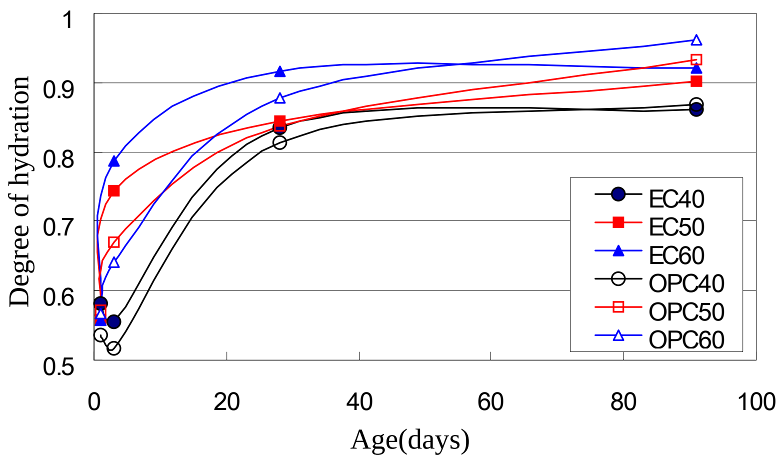

Fig.4 Degree of hydration of cement measured by image analysis

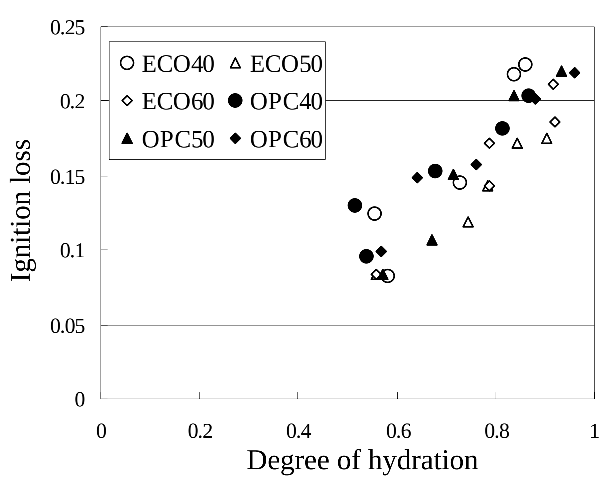

Fig.5 Relationship between degree of hydration and ignition loss

The calculation result of the degree of hydration of cement calculated by the equation (1) is shown in Fig.4. At early age, degree of hydration of eco-cement is higher than that of OPC in each W/C. However, that of OPC is higher than that of ECO at 91days. Fig.5 shows the relation between the degree of hydration and the ignition loss. It was shown the degree of hydration and the ignition loss is in a good correlation. At the same degree of hydration, the ignition loss of ECO indicated some high values from OPC.

3.3 Pore structure measurement result by mercury intrusion method

Fig.6 shows the measurement result by MIP. The amount of a total pore volume in both cements decreases greatly from 7 to 28day. At 91days total pore volume of ECO in every W/C is higher than that of OPC.

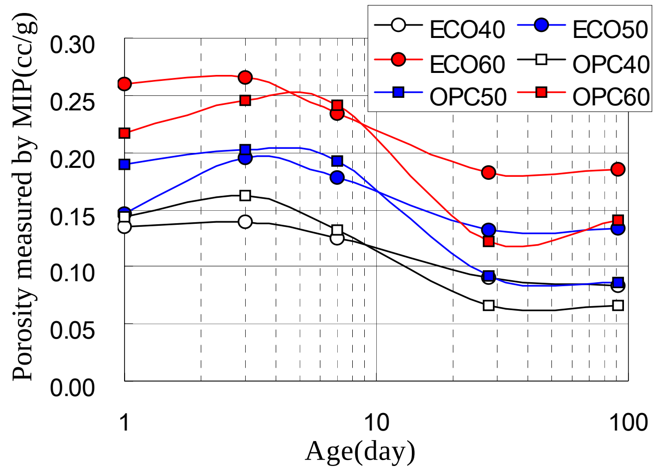

Fig.6 Porosity measured by MIP

4. Discussion

Fig.7 shows the relation between the degree of hydration and compressive strength. As for the degree of hydration and compressive strength, they are in the proportion and both of cements tendency were also the same in each W/Cs. In other word, it was suggested that the degree of hydration of cement greatly influence in the development of compressive strength in ECO as well as OPC.

Fig.8 shows the relation between the amount of a total pore volume measured by MIP and compressive strength. As for the relation between the amount of the total pore volume larger than 50nm in diameter and compressive strength, a roughly good correlation was shown. It was not a good correlation in the range where the amount of the porosity was a little though it was a good correlation in the range where the amount of the porosity was large.

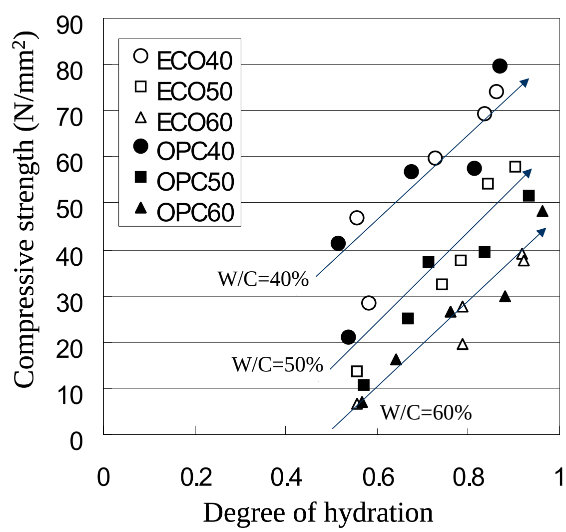

Fig.7 Effect of degree of hydration of cement on strength

Fig.9 shows the relation between the amount of porosity measured by image analysis and compressive strength. As for the relation between the amount of the porosity larger than 0.32μm in diameter and compressive strength, a good correlation was shown. The compressive strength rose greatly with decrease of porosity in the range of the amount of the porosity was a little. A result of MIP is similar to that of image analysis. In a word, it was shown that either cement also greatly depended on the amount of the larger porosity for compressive strength. A big difference could not be seen between the result of eco-cement and OPC. Therefore, it was shown that the strength of eco-cement did not increase at the later age because the hydration of cement ended almost in early age and it was not able to decrease the porosity. However, after the 28day, the strength increased though the hydration of cement is finished almost, and the amount of the porosity hardly changes either.

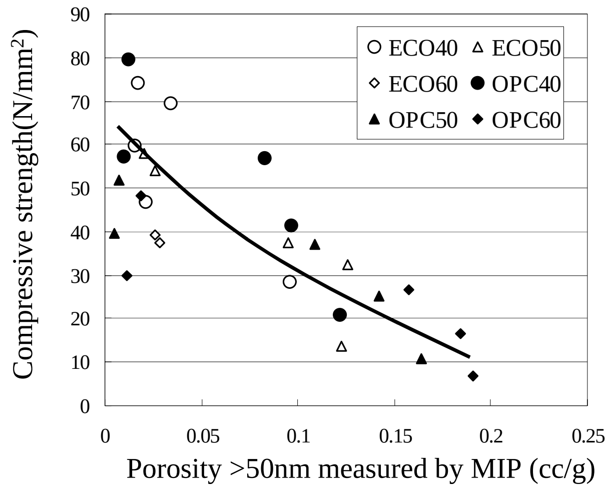

Fig.8 Effect of large pore on compressive strength

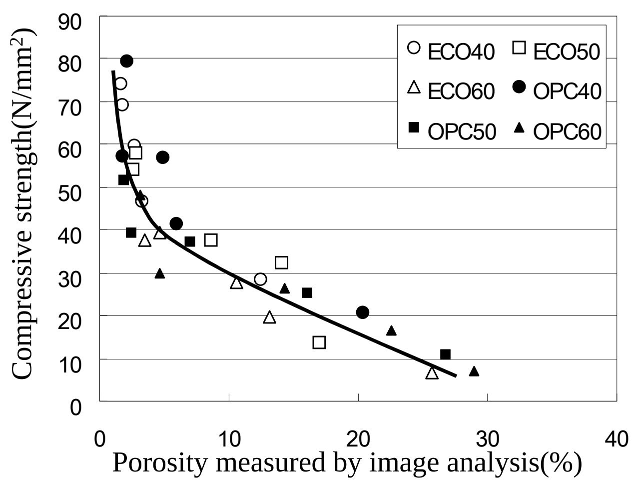

Fig.9 Effect of porosity measured by image analysis on strength

4.1 Micro elastic modulus of CSH measurement by Indentation method

Figure 10 shows the surface of the sample after measured by the Indentation method. A black square part was measured by Indentation, and the composition of each point is analyzed by EDX. Fig.11 shows the result of

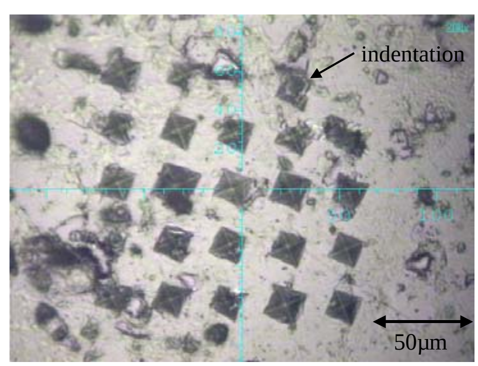

Fig.10 Measurement of indentation

measuring the elastic modulus of CSH by the Indentation method. The elastic modulus of CSH of OPC increased from the 28th to the 91day. However, the elastic modulus of CSH of eco-cement differs from OPC, and has not increased from the 28 to 91days so much. Because eco-cement has larger amount of ettringite and monosulfonate that are weaker than CSH than that of OPC at later age.

Fig.12 shows the effect of micro elastic modulus of CSH on compressive strength. There is a good correlation between micro elastic modulus of CSH and compressive strength. It was shown that CSH is occupied large volume in paste, therefore, it greatly influenced on strength.

4.2 CaO/SiO_2 molar ratio measurement

The point of specimens is analyzed by using EDX and the result of calculating the molar ratio of CaO/SiO_2(C/S) of CSH is shown in Fig.13. It was a tendency to decrease with the increase of age regardless of OPC and eco-cement. However, it was shown that C/S of CSH in eco-cement was always higher than that in OPC.

Fig.14 shows the relation of the micro elastic modulus and C/S molar ratio of CSH. A micro elastic modulus decreased with an increase of C/S, and a very good correlation of C/S and micro elastic modulus was seen by both in OPC and ECO. It was

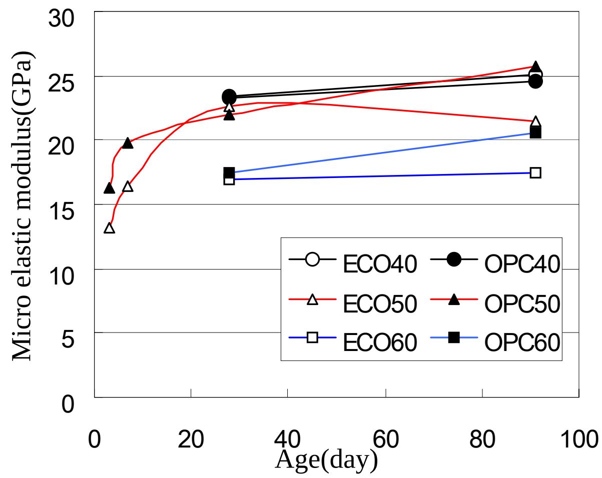

Fig.11 Micro elastic modulus of CSH measured by indentation

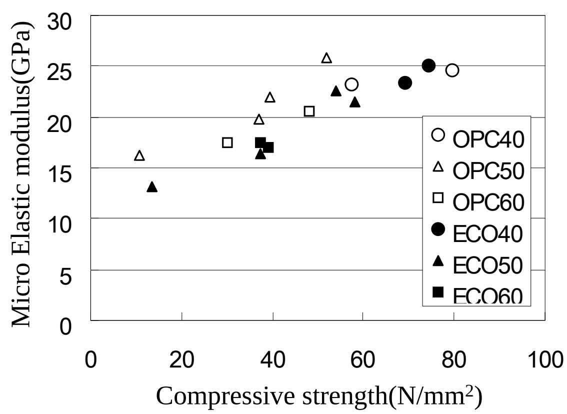

Fig.12 Effect of micro elastic modulus of CSH on strength

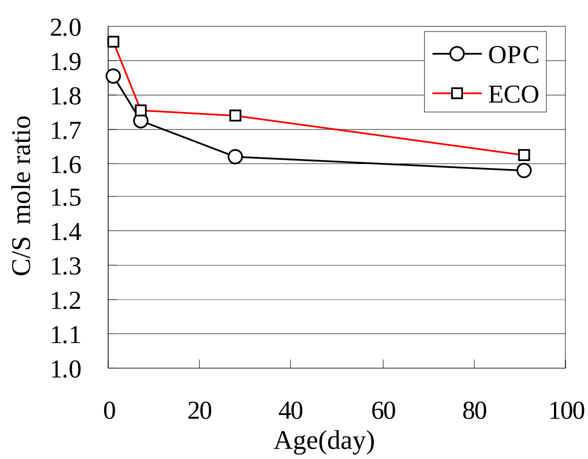

Fig.13 CaO/SiO_2 mole ratio of CSH in OPC and ECO(W/C:0.5) shown that the elasticity behavior depends on the composition of CSH. It is thought that the strength of eco-cement has not increased so much in later age because C/S of CSH is somewhat higher than that of OPC.

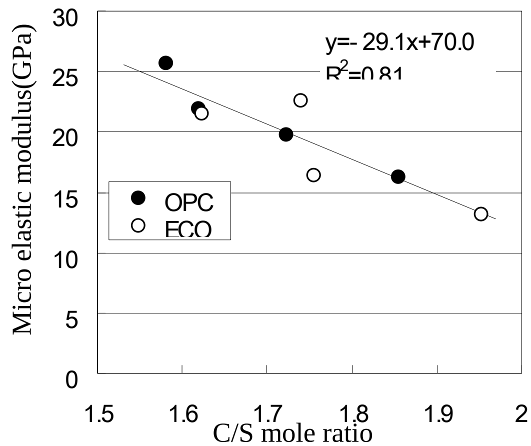

Fig.14 Effect of C/S of CSH on micro elastic modulus

5. Summary

It was clarified that a different hydration products was produced in eco-cement and OPC by BEI and EDX measurement. An increase in strength was not seen at later age though the strength development of eco-cement in early age is large. This is thought that it is because Belite is not so included in eco-cement though it included a lot of Aluminate. A needle shape product was observed, and it was shown that the part was not a too dense structure in eco-cement even on the 28days. A different result was obtained from the measurement of a micro elastic modulus in eco-cement and OPC, and the micro elastic modulus development of eco-cement in later age is not seen.

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