

Analysis on Calcination of Cementitious Powder of Waste Concrete for Raw Cement

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Abstract

The purpose of this study is to examine whether cementitious powder separated from waste concrete can be used as an alternative raw material to limestone and reduce the usage of natural resource (limestone) and CO₂ emission based on recycling cementitious powder from waste concrete. Experiments actually analyzed the chemical composition of cementitious powder and performed hyperthermia analysis, measurement of free CaO and XRD analysis to measure the degree of recovery of hydration in the model of cementitious powder manufactured based on chemical composition. These were performed in each cementitious powder model at different calcination temperatures such as 900°C, 1200°C, 1300°C, 1400°C and 1450°C. Through the experiments, it was found that the recovery of hydration was at a level which can be used as the alternative raw material for limestone, but the replacement ratio was directly affected by the degree of mixing of fine aggregate in less than 150 μm, which cannot be separated from cementitious powder. It was shown that there was no difference in the production of compounds involved in hydration at calcination temperatures of 1200°C or higher. Therefore, to pursue the replacement of limestone and reduction of greenhouse gas by recycling cementitious powder, the development of technology to efficiently separate aggregate fine powder is required.

Keywords : cementitious powder of waste concrete, recycled cement, powder of fine

1. Introduction

Measures for recycling waste concrete, which accounts for more than 60% of construction waste, are actively being studied these days in order to minimize the environmental load occurring in construction and in the construction process of eco-friendly structures. Through this process, the study reaches the practical stage to manufacture and reuse cyclic aggregate with high quality through a

variety of recycling processes[1,2]. In addition, some studies to recycle the fine grain containing fine aggregate produced after manufacturing cyclic aggregate and the cementitious powder of paste ingredients in which fine aggregate ingredients are removed are being conducted. In such cases of recycling cementitious powder it was generally used as an alternative for silica flour in the manufacture of cement series products such as roadbed ash as inert filler or brick. Some studies are being conducted with the goal of utilizing recycled cement through low-temperature calcination process[3,4].

The amount of CO₂ emission depending on decarbonation of limestone compared with the total CO₂ emission was 67.5%. The amount of CO₂ emission depending on combustion was 26.7% and CO₂ emission

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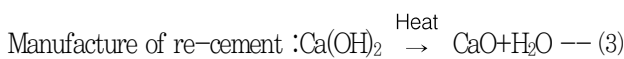
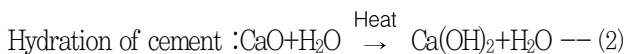
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depending on electric power in plants was 5.8%. Therefore, it was evaluated to be very significant in the reduction of greenhouse gas.

In this study, we would like to use the large amount of paste ingredients included in cementitious powder of waste concrete (consists of cement hydrate in which coarse aggregate and fine aggregate more than 150 μm are removed through recycling process of waste cement, and some fine aggregate cementitious powder; hereinafter, called waste cementitious powder) as an alternative raw material to limestone.

In this case, it is expected to have the effect of saving natural resources as a substitute for limestone, and reduce the greenhouse gas emissions caused by decarbonation reaction of limestone, according to the mechanism for hydration reaction of cement and recycled cement as shown in equations (1), (2) and (3).

Thus, this study analyzed the possibility of the use of waste cementitious powder mixed with cementitious powder of fine aggregate as raw material (Limestone) for cement through the optimal combination of cement raw material. In addition, we analyzed the possibility of saving limestone raw material through this process[5].



2. Materials used

This study manufactured model waste cementitious powder and used it as raw material for experiment based on the chemical compositions of actual waste cementitious powder. Since formulation and age of

waste cementitious powder in each site were unknown and these values were not consistent, it was determined to be inappropriate for a comparative analysis on the addition ratio of fine aggregate and calcination temperature. The model waste cementitious powder used paste aged 6 months and fine aggregate less than 150 μm based on previous studies. In addition, converter slag, which has high iron content, was used to coordinate IM as an ingredient adjuster. Chemical compositions of the model waste cementitious powder and byproduct raw materials used in this study are shown in Tables 1 and 2.

Table 1. Chemical compositions of model waste cementitious powder

Classification	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
Paste	47.70	18.20	3.86	2.63	0.00
Fine aggregate	1.32	75.10	12.10	2.03	0.00

Table 2. Chemical compositions of each raw material and ingredient adjuster

Classification	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
Limestone	45.20	11.15	2.04	0.81	0.20
Converter Slag	31.80	14.90	2.74	38.40	0.11

3. Experimental methods

In this study, actual waste cementitious powder was first collected from 11 sites nationwide in Korea and the chemical composition of the samples was analyzed. The addition ratio of fine aggregate was estimated through comparison with Portland cement by using the SOLVER add-in in Excel using the principle of GRG (Generalized Reduced Gradient) Methods, and the model waste cementitious powder was generated. At the same time, the effect on the use of fine aggregate added to the waste cementitious powder as an alternative material for limestone was investigated. Multiple optimization for the combination of raw materials was performed to make

recycled cement by using SOLVER add-in in EXCEL with converter slag utilizing waste cementitious powder as an alternative material for limestone[6]. Raw material adjustment factor range was LSD (Lime Saturation Degree: $(CaO - 0.7 \times S O_3) / (2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3) \times 100$) of 87.0, SM (Silica Modulus: $SiO_2 / (Al_2O_3 + Fe_2O_3) \times 100$) of 3.0 and IM (Iron Modul: $Al_2O_3 / (Fe_2O_3) \times 100$) of 1.10 on the basis of moderate heat cement with low LSD and high SM in order to maximize the amount of use of waste cementitious powder including large amount of SiO_2 [7]. In order to determine the degree of recovery of hydration of recycled cement, in this study, TG/DTA thermal analysis, Free CaO measurement, and X-ray diffraction analysis were performed. These were performed at different temperatures such as 900°C, 1200°C, 1300°C, 1400°C and 1450°C in order to determine the degree of recovery of hydration at each calcination temperature. Experimental items, experimental factors and levels are shown in Tables 3 and 4 below. The manufacturing process of clinker, model cementitious powder, used in this experiments is shown in Figure 1.

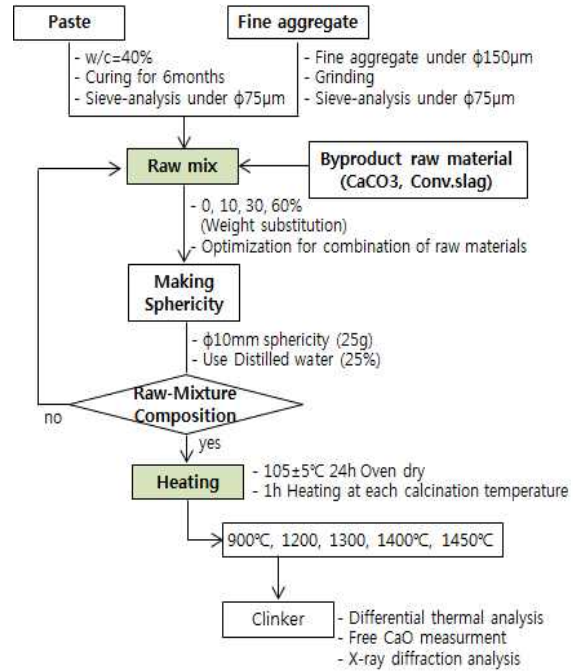


Figure 1. Flow chart of the manufacture of recycle cement model

4. Experimental results and analysis.

4.1 Chemical compositions of actual waste cementitious powder.

The results of an analysis on the chemical compositions of actual waste cementitious powder are shown in Table 5. Comparisons with the chemical composition of Portland cement are shown in Figure 2. As shown in Figure 2, chemical composition of actual waste cementitious powder had approximately 30% more SiO_2 , approximately 5% more Al_2O_3 , approximately 43% less CaO and approximately 0.6% less Fe_2O_3 compared with the levels found in Portland cement. This is thought to have been caused by the inclusion of cementitious fine aggregate which cannot be completely separated because of the similar grain size.

Through an analysis based on chemical compositions of fine aggregate in Table 1 and the chemical composition of original Portland cement in Table 6, it was found that the mean of chemical composition of actual waste cementitious powder showed the most

Table 3. Experimental factors and levels

factor	cementitious powder model (%)	Manufacturing recycle prste		
		Firing temperature (°C)	Firing time (min)	Raw material of OPC
Level	S/M 65	900 1200 1300 1400 1450	60	Lime stone conv.slag
ea	1	5	1	1

Table 4. Experimental item

Experimental Item	Note
Stability of clinker	X-ray diffraction KS M 0043
Hydration property	Thermal analysis (TG/DTA) Free CaO KS M ISO 11358 -

similar degrees of addition of 65% of fine aggregate in all conditions to the addition ratio of fine aggregate. Despite a slight difference in the two values, all values of addition of 65% of fine aggregate are included in the actual waste cementitious powder. Chemical compositions of waste cementitious powder model with fine aggregate are shown in Table 6.

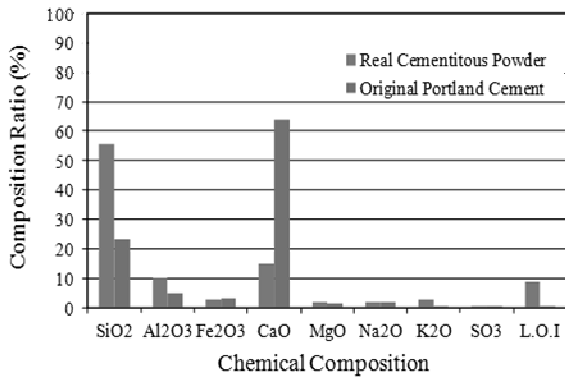


Figure 2. Comparison of chemical composition of actual waste cementitious powder and original Portland cement

Table 5. Chemical composition of actual waste cementitious powder

Classification	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
1	13.7	58.6	10.3	2.2	0.4
2	15.2	56.1	10.3	2.8	0.5
3	15.0	58.0	9.7	2.9	0.5
4	15.1	56.2	10.2	2.7	0.6
5	15.9	50.9	12.5	3.8	0.6
6	16.6	54.1	10.3	3.3	0.5
7	14.5	60.2	9.2	2.7	0.5
8	14.3	57.6	10.2	3.2	0.4
9	13.8	58.2	10.5	2.8	0.5
10	14.9	56.3	10.3	3.0	0.4
11	17.4	47.8	8.7	2.4	0.5
Mean	15.1	55.8	10.2	2.9	0.5
Portland Cement	63.8	23.1	5.0	3.0	0.5

Table 6. Chemical composition of waste cementitious powder models

Classification	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃
Fine aggregate 50%	24.5	46.7	8.0	2.3	0.0
Fine aggregate 60%	19.9	52.3	8.8	2.3	0.0
Fine aggregate 65%	17.6	55.2	9.2	2.2	0.0
Fine aggregate 70%	14.2	59.0	9.6	2.2	0.0
Fine aggregate 80%	10.6	63.7	10.5	2.2	0.0

4.2 Combination of raw materials based on the addition ratio of fine aggregates

Combinations of raw materials were made in increments of 10% within the range of a 0%–90% addition ratio of fine aggregate. As shown in Figure 3 and Table 7, as the addition ratio of fine aggregate was increased, the replacement ratio of waste cementitious powder for limestone was dramatically decreased. In particular, the waste cementitious powder model with a 65% addition ratio of fine aggregate could be used as the alternative raw material for limestone at the level of 9.52%. This was because it was difficult to fully synthesize to C₃S and C₃A because the amount of SiO₂ is increased and ingredients of CaO and Al₂O₃ were decreased in waste cementitious powder due to the addition of the ingredient of fine aggregate. At the time, it was shown that the possibility of using SiO₂ as an alternative for clay of quartz rather than limestone was increased. Thus, to increase the utilization of the waste cementitious powder with high added value, it is thought that the grinding technology to efficiently separate fine aggregate from cement hydrates should be developed.

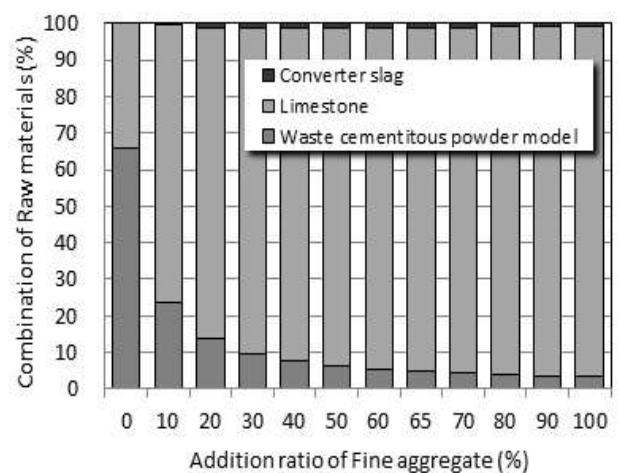


Figure 3. Combination of raw materials based on addition ratio of fine aggregate

Table 7. Combination of raw materials based on addition ratio of fine aggregate

(Unit: %)				
Addition ratio of fine aggregate	Waste cementitious powder model	Limestone	Converter slag	Ignition loss
0	81.76	15.78	2.46	24.82
10	37.55	58.97	3.48	30.00
20	24.37	71.84	3.78	31.55
30	18.04	78.03	3.93	32.29
40	14.32	81.66	4.02	32.73
50	11.87	84.06	4.07	33.01
60	10.14	86.04	3.82	33.22
65	9.52	86.58	3.90	33.36
70	8.85	87.01	4.14	33.37
80	7.85	87.99	4.17	33.49
90	7.05	88.77	4.18	33.58

4.3 Free CaO measurement

Figure 4 shows the result of measurement of the contents of Free CaO at 900 ~ 1450°C. As shown in the Figure, as the calcination temperature was increased, the content of free CaO was decreased. However, content of free CaO was reduced to 0.2~0.5% or almost became extinct at calcination temperatures of over 1450°C. However, for clinker used in this study it showed more than 2%, which was significantly high. In addition, Burnability (BI) was calculated as 40.96, which was somewhat lacking when compared with the levels in existing studies of 48~52. It was thought that the SiO₂ included as the form of Quartz crystal caused in fine aggregate had low reactivity with CaO.

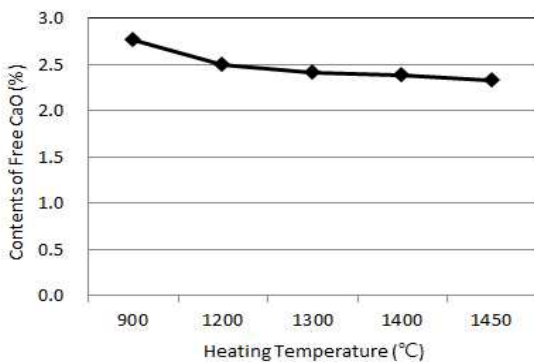


Figure 4. Free CaO of clinker with each firing temperature

4.4 Differential thermal analysis.

To determine the reactivity of combined raw materials, differential thermal analysis was conducted and the results are shown in Figure 5. The temperatures at which major reactions occurred were shown in Table 8. The formation and decomposition of compounds confirm generally suitable temperatures.

After adherent moisture of clay minerals was vaporized at 452.05°C, endothermic peak caused by decarbonation of limestone was observed at 763.63°C. Exothermic peak caused by C₂S was observed at 1272.9°C. In addition, endothermic peak caused by formation of liquid phase of C₃A and C₄AF was observed at 1354.74°C. Thermal decomposition temperature of limestone was determined to be relatively low when compared with results of the study of Ahn, Ji Whan et al. The reason was that L.S.D. was set at 87, which was a low level, as moderate thermal cement was mixed with raw material. When compared with the results of the study conducted by J. A. Imlach et al., C₃A and C₄AF formed liquid phase at a relatively high temperature, because it was mixed at S.M. of 3.0, a high level. In addition, CaCO₃ decomposition reaction was 39.93% at 763.63°C, which was similar to the previous study.

Table 8. Differential Thermal Analysis of waste cementitious powder model raw material

	CaCO ₃ decomposition	C ₂ S formation	Liquid phase
Temperature(°C)	763.63	1272.9	1354.74

4.5 X-Ray diffraction analysis.

XRD pattern of clinker at each calcination temperature is shown in Figure 6. As shown in the Figure, a large amount of SiO₂ and CaO, which did not have any reactivity at 900°C, existed, and β-C₂S phase, which was some linker mineral phase, appeared slightly. However, the major ingredients did not seem to be reactive yet. Despite this, it was shown that

clinker calcinated at over 1200°C produced C₃S and β-C₂S as diffraction peaks of SiO₂ and CaO were reduced. In the case of C₃A, diffraction peaks were shown at 1300 and 1400°C, but became extinct at 1450°C.

In general, the amount of C₂S reached a maximum at 1200°C. As the liquid phase began to be generated at 1250°C, the reaction of C₂S and CaO was facilitated so that the amount of C₃S tended to increase. However, the amount of C₂S and C₃S was constant at over 1200°C, because the cause was thought to be the same result found in Free CaO analysis.

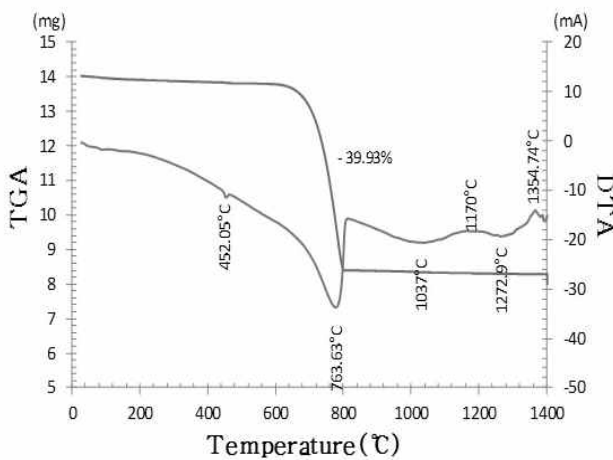


Figure 5. TG-DTA curves of raw material

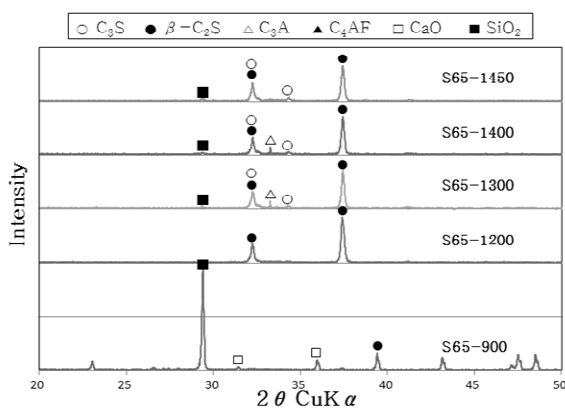


Figure 6. XRD pattern of clinker with each firing temperature

5. Conclusions

The following conclusions were obtained through the above experiments.

- 1) Through the analysis of the chemical compositions of cementitious powder of waste concrete, CaO and SiO₂ are found to be the main ingredients, as had been shown in the existing studies. Content of CaO is significantly decreased but content of SiO₂ is significantly increased. Mix ratio of fine aggregate and fine powder is found to be approximately 65 %.
- 2) By attempting to chemically optimize recycled cement for multi-purpose use, it is found that cement of moderate heat with values of LSD:87, SM:3, IM:1.1 can be produced. It is found that the replacement rate of cementitious powder for limestone is dramatically reduced when the mixing ratio of fine aggregate is increased.
- 3) In the differential thermal analysis of the composition of raw materials, exothermic peak caused by C₂S formation is observed at 1272.9°C. Endothermic peak caused by formation of liquid phase is observed at 1354.74°C.
- 4) The analysis of free CaO showed that the content of free CaO is reduced with increasing calcination temperature. However, it has a relatively low burnability of 40.96.
- 5) Through X-ray diffraction analysis of the recycled cement, it was found that compounds composed of cement such as C₂S, C₃S and C₃A can be synthesized. However, there is no significantly big change at 1200°C or higher.

The investigations described above showed that recycled cement can be utilized as an alternative raw material to limestone. However, to increase the replacement ratio, fine powder of fine aggregate should

be efficiently separated from the waste cementitious powder.

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