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Hydration Analysis of Fine Particle and Old Mortar Attached on the Surface of Recycled Aggregate

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Abstract

When recycled aggregate with old mortar and particles is used in concrete mixing, such aggregates can affect hydration reaction by promoting or inhibiting it. In this study, the possibility of hydration reaction on old mortar and particle was analyzed. Hydration reaction was carried out in old mortar that is finely crushed by an impact machine in the production of recycled aggregates, and it was found that this did have an impact on the strength development of concrete. Unlike in old cement, the hydration reaction did not progress in the particles, and it had high amounts of silica powder and calcium carbonate. In conclusion, the old mortar can have the influence of improving compressive strength, but the particles can delay the setting time of recycled aggregate concrete.

Keywords : recycled aggregate, old mortar, fine grained, hydration, differential scanning calorimetry

1. Introduction

1.1 Research objective and background

The recycled aggregate generated using a strike–back type jaw crusher has old mortar on the surface, although it differs in terms of the volume and the area attached of mortar, depending on its characteristics. The sizes of cement particles usually range from 5㎛ to 55㎛, and the depth of cement particles hydrated for about 1 year stands at around 9㎛[1]. Since the hydration reaction thickness of cement is about 25㎛, there might be an interior core of unhydrated cement even though the cement appears as though it has already hydrated[2].

When produced in the strike–back type, the recycled aggregate leaves a lot of fine particles on the surface after hydration due to some wear of cement caused by abrasion between aggregates in the course of production or impact, causing the unhydrated cement to expose externally. The unhydrated cement particles exposed like this could initiate a hydration reaction with water, for which the possibility of recycling it as recycled cement has actively been studied[3,4]. According to the aforementioned studies, the unhydrated cement particles attached to recycled aggregate could initiate a hydration reaction, which could have an influence on the strength of concrete by increasing the unit volume of cement.

This study aims to analyze the possibility of hydration of old mortar and fine particles using differential scanning calorimetry (DSC) developed by Sha et al.[5] to understand the influence on changes in strength of recycled concrete.

2. XRD and DSC experiment plan and method

To analyze hydration and component of old mortar

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and fine particles attached to recycled aggregate, the specimen was prepared as indicated in Table 1.

Table 1. Specimens for XRD and DSC analysis

Type	Old cement mortar	Fine grained
XRD	-	• Dried fine grained • Fine grained + water
DSC	• OPC • Old cement mortar • Old cement mortar + water	• Dried fine grained • Fine grained + water

2.1 Manufacturing of specimen for XRD analysis

Figure 1 indicates the manufacturing process of the specimen for the analysis of fine particles from recycled aggregate. Ultrasonic cleaning was done for 1 hour at 80℃ to separate the loose particles from the surface of recycled aggregate. Kerosene was used as cleaning solution to control the initial reaction between fine particles and water. The fine particles on the floor of the cleaning machine were dried at 100℃after the cleaning, and then filtered out using a 100 micron test sieve. XRD of the fine particles gathered through the 100 micron test sieve were analyzed before and after hydration reaction (at 28 days).

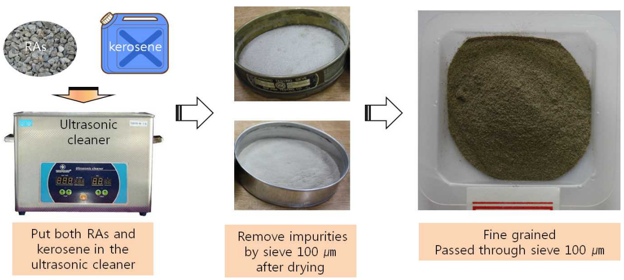

Figure 1. Specimen for XRD analysis of fine grained

2.2 Differential Scanning Calorimetry (DSC)

Ordinary Portland cement consists of four main components that can react with water: C3S, C2S, C3A, and C4AF. C3S and C2S are reacted with water, generating calcium silicate hydrate (C-S-H) and CH. Therefore, if there is still hydration potential in old mortar and it is activated by water, the four components mentioned above will be formed, leading to thermal changes by heat absorption or heat generation.

Thermal analysis is a means of testing changes in physical and chemical characteristics such as weight, changes of enthalpy or heat content, which are recorded in a heat or time function. Depending on the parameter to be measured, thermal analysis can be performed through one of the following methods: differential thermal analysis (DTA), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC), which has generally been used to measure cement hydration products [6,7,8].

In this research, differential scanning calorimetry (DSC), in wide use for studies on the properties of material, was used due to its capacity for rapid, high-precision analysis of changes in the heat of material. In the analysis of a high molecule substance, crystallization temperature (Tc), melting temperature (Tm) and glass transition temperature (Tg) are indicated. Therefore, DSC, which can measure changes in thermal energy according to temperature change, is widely used in studying high molecular substances, and offers the advantage of allowing researchers to obtain accurate analysis results quickly. More detailed information can be found in the studies done by Murakami et al.[9] and Chou and Bhadeshia[10].

2.3 Manufacture of specimen for DSC analysis

2.3.1 Old mortar specimen for DSC analysis

The old mortar specimen for thermal analysis shown in Figure 2 was detached from the surface of recycled aggregate and then crushed. However, as the fine particles, the main material for recycled cement, usually obtained from the cement component, CaO and SiO_2 are the main components. CaO was

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largely decreasing while SiO_2 was doubled when mortar or waste concrete was used as the basic material. This is because a lot of fine particles of aggregate are included in the process of manufacturing recycled cement[4,11].

First of all, if the recycled aggregate is crushed and included by impact when the old mortar from the recycled aggregate is crushed, it is possible for fine particles of the aggregate to affect thermal analysis. For this reason, the old mortar from the aggregate was crushed coarsely and filtered through a 300 micron test sieve to separate the aggregate. Next, the old mortar sifted was crushed finely again using a ball, andsifted through a 150 micron test sieve to use old mortar only. The old mortar sifted through the 150 micron test sieve was mixed with water in the weight ratio of 1:0.5, and then cured for 7 days and 14 days to conduct a thermal analysis.

The specimen was prepared in three types: new cement paste consisting of ordinary Portland cement was mixed with water, old mortar separated from recycled aggregate, and old cement paste hydrated by adding water to old mortar separated from recycled aggregate.

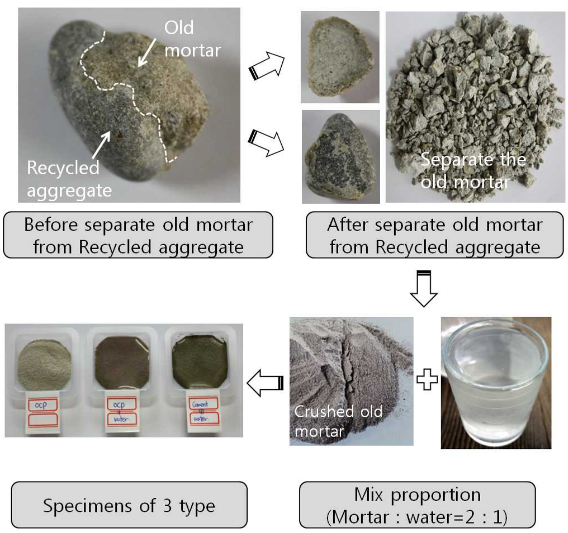

Figure 2. Specimens for DSC analysis

2.3.2 Fine particle specimen for DSC analysis

The fine particle specimen on the surface of the recycled aggregate for a thermal analysis was prepared in two types, as shown in Figure 3: dried fine particles and fine particle paste. The fine particle paste was prepared by mixing dried fine particles with water in the weight ratio of 1:0.5. The thermal analysis of the specimen was performed at 14 days.

Figure 3. Specimen for DSC analysis of fine grained

2.4 DSC Test Method

2.4.1 DSC test method

The test rig used in this test was SDT Q 600DSC instrument, a simultaneous TGA/DSC analyzer. The volume of sample to be loaded on the hold for a test is less than 40mg. In this study, around 20mg was set as the test volume. The entire specimen was heated under dry nitrogen (N_2) at a heating rate of 10℃/min until the heat reached 1000℃.

3. Results of XRD and DSC analysis of old mortar and fine particles

3.1 Chemical component analysis of old mortar

Table 2 indicates the chemical component of old mortar separated from recycled aggregate. The chemical component of the old mortar separated from recycled aggregate used in this study was compared with that of the recycled cement used by other researchers. The content of SiO_2 and Al_2O_3 was reported to be 21.63% and 9.81%, respectively, by Spoon et al.[12], which was similar to the analysis results of this study.

In addition, the SiO_2 content of the specimen used in this study was shown to be similar to that of the OPC but less than that of the basic material for mortar used in the previous studies, including the study of Ahn et al.[13]; on this basis, it is believed that the fine particles used as specimen in this study obtained from old mortar attached to recycled aggregate were separated satisfactorily.

Table 2. Chemical component of cement powder according to type

Type	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	insol.
OPC	64.2	22	5.1	3.1	1.5	0.8
Paste*	56.7	17.2	4.5	2.5	2.4	-
Mortar*	37.9	42.9	3.9	2.47	2.52	32.5
Old mortar used in this study	34.85	26.17	8.02	1.92	2.33	24.71

*Reference [11]

3.2 XRD analysis results

As shown in Figure 5, a small amount of Etringite and hydrated potassium generated in the process of hydration were found in OPC. In some cases, the main component of the cement was found to be calcium silica gate.

However, there were no big differences found in the fine particles separated from recycled aggregate before and after mixing water. $CaCO_3$ was identified, which could be substantial proof of reaction of silica powder (SiO_2), the sand component, detaching from the cement mortar or paste, with CO_2 in the air.

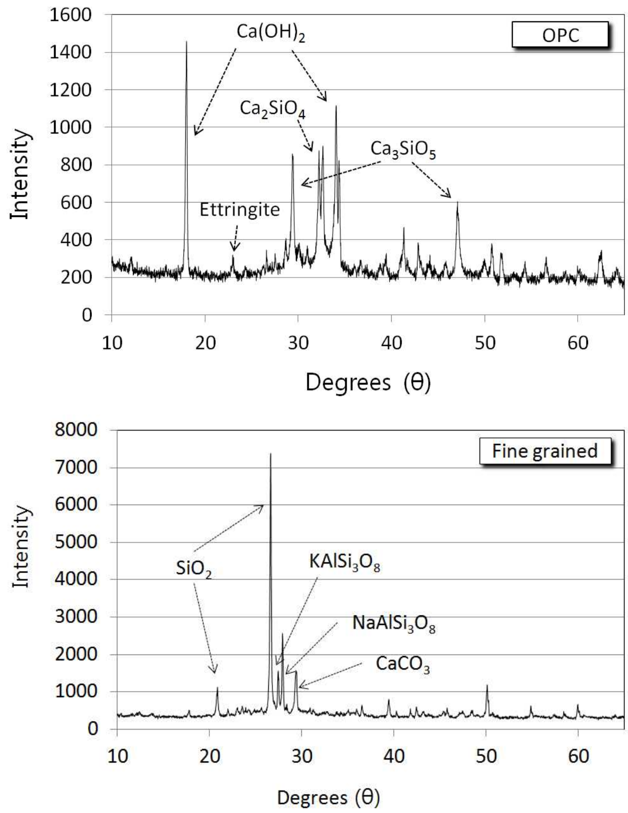

Figure 4. XRD for the fine grained

Through the XRD analysis results, a lot of SiO_2 was included in the form of fine particles detaching from aggregate in the course of manufacturing of recycled aggregate due to crushing or wearing. This is known to form alkali silicate gel through reaction with alkali properties such as NaOH and KOH in the cleaning solution for concrete. When the alkali silicate meets water, an alkali silica reaction occurs. A series of this reaction could give rise to the potential for cracks and pop-out in the recycled concrete in the future, which may cause a deterioration in the durability of recycled concrete. SiO_2, which is present to a high degree in the fine particles, tends to cause swelling by creating alkali-silica reaction gel alongside pozzolanic reaction. Recycled aggregate could increase in alkali due to unhydrated old mortar and fine particles, which could result in drying shrinkage crack due to alkali-silica reaction[14].

However, copper slag causes a pozzolanic reaction

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that increases the consumption of calcium hydroxide and generates more C-H-S, which can control the swelling caused by alkali-silica reaction[15,16]. For this reason, it is believed that copper slag is appropriate as an admixture for recycled concrete to control the alkali-silica reaction.

3.3 DSC analysis results of old mortar

In the case of concrete, as indicated in Table 3[13], dehydration and water evaporation take place at a low temperature, while disruption and decomposition take place at a high temperature. Dehydration reaction of $Ca(HO)_2$ is found between 400-600℃ while decarboxylation reaction of $CaCO_3$ is found between 600-900℃.

Table 3. Change characteristics of concrete according to temperature variation

Temperature(℃)	DSC-TG	Change characteristics
Room temperature ~100	Water evaporation	· Evaporation of free water such as absorbed water, gel water and capillary water · Chemically stable state
100~400	Disruption of cement hydration and gel	· Dehydration of hydrate in Al_2O_3, Fe_2O_3 and Tobermoriter gel · $(CaO)_3SiO_2 \cdot CaSO_4 \cdot nH_2O \rightarrow (CaO)_3SiO_2 \cdot nH_2O \uparrow$
400~600	Decomposition of calcium hydroxide in 481.7℃ (endothermic reaction)	· Decomposition of $Ca(OH)_2$ $Ca(OH)_2 \rightarrow CaO+H_2O \uparrow$
600~900	Almost no weight change by decarboxylation in 60.3℃	· Decomposition of $CaCO_3$ $CaCO_3 \rightarrow CaO+CO_2 \uparrow$

Figures 5 and 6 show the DSC analysis results of cement mortar; the peak at the upward peak is endothermic reaction and the downward peak is exothermic reaction. Identical peaks were shown at identical temperatures at 7 days and 14 days. The intensity at 14 days was stronger than that at 7 days.

The first peak was due to dehydration of free water from within C-S-H. There was dehydration of water from within C-S-H found in the old cement paste made by adding water to old mortar, though this was small compared to the new cement paste made by adding water to OPC.

The second peak is calcium hydroxide ($Ca(OH)_2$). As age increased, the intensity of calcium hydroxide was indicated to be stronger, which is because more C-S-H and $Ca(OH)_2$ were generated by hydration reaction. The intensity was shown to be similar in old and new cement paste. However, there was no intensity found in the old mortar separated from recycled aggregate. It is believed that the hydrated parts of cement may have been separated or worn by crushing or impact among aggregate in the manufacturing process of recycled aggregate, as mentioned previously, or it reacted with CO_2 on an open-air storage yard, turning into $CaCO_3$. In other words, through the thermal analysis it was proven there are unhydrated cement particles in the old mortar, which could react with water, though with a weak peak of $CaCO_3$ compared to that of new cement paste.

The third peak is $CaCO_3$ generated from the reaction between $Ca(OH)_2$ generated through hydration process and CO_2 in the air. It was shown to be similar in the three specimens at each curing day. In terms of intensity of the peak by specimen, old and new cement paste was shown to be similar, while old mortar was shown to be stronger than the other two specimens in terms of the intensity of $CaCO_3$. That is, the reason why the intensity of $CaCO_3$ was shown to be stronger in old mortar may be that the $Ca(OH)_2$ generated through hydration reaction was exposed in the air for a long time, during which it was combined with CO_2, turning into $CaCO_3$, and old mortar held more $CaCO_3$ than old cement paste.

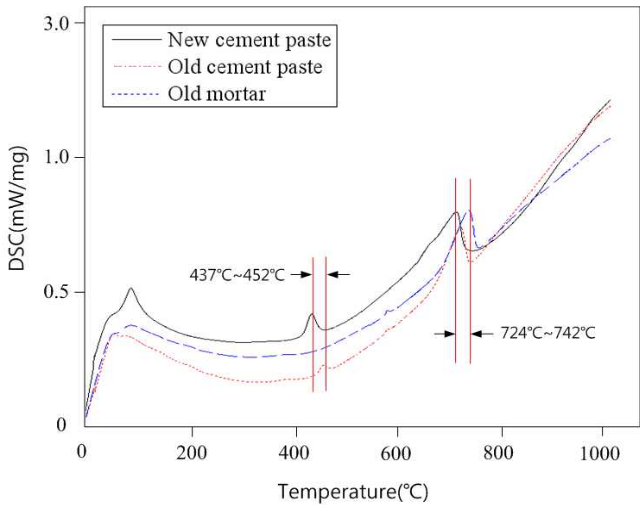

Figure 5. DSC curve of old cement paste(curing ages 7 days)

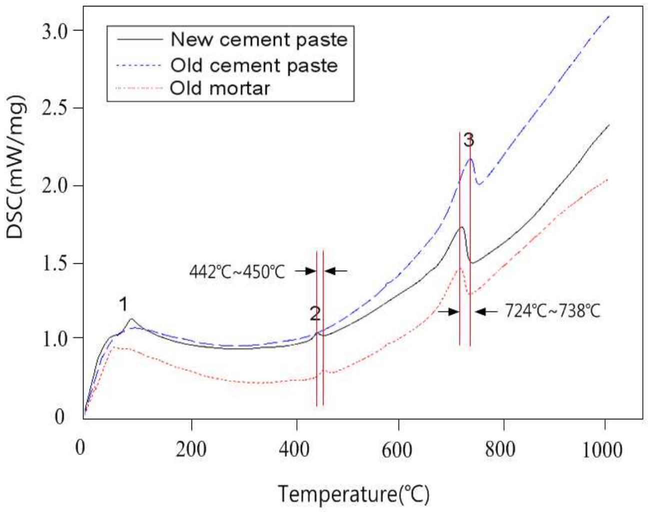

Figure 6. DSC curve of old cement paste(curing ages 14 days)

Surface are likely to be worn by impact or friction between aggregates, and unhydrated cement particles could be exposed on the surface, which means the old cement on the surface of the recycled aggregate could be hardened due to a reaction with water. When the old cement mortar reacts with water, it is possible for the old cement on the surface of the aggregate to increase the unit cement volume due to the old cement mortar, intensifying the concrete accordingly.

However, the initial strength was developed more rapidly, while the long-term strength was developed slowly compared to OPC[17], and the final strength is usually not as strong as that of OPC. Despite the increase in the unit volume of cement, the long-term strength was lower, which might be because it held a small amount of unhydrated cement particles, and the influence on strength was small.

In addition, it is believed that micro-cracks within the recycled aggregate, deterioration by the old cement mortar on the surface of the recycled aggregate, and decrease in the unit quantity by water absorption had a greater influence on the strength than the increase in strength caused by unhydrated cement particles, which means it can improve initial strength development while deteriorating long-term strength.

To minimize a decrease in the long-term strength development when using recycled aggregate, it is necessary to study concrete mixture with blast-furnace slag or copper slag in the future.

3.4 DSC analysis results of fine particles

As illustrated in Figure 7, fine particles and fine particle paste were analyzed to have one peak at around 700℃, and cement paste was analyzed to have three peaks, each of which was shown at 100℃ and 450℃, respectively, and so was at 700℃. The first peak was caused by dehydration reaction of free water from within C-S-H, the second peak is $Ca(OH)_2$, the cement hydration product, and the third peak is $CaCO_3$.

There were no hydration products such as C-S-H and $Ca(OH)_2$ found, both in fine particles and in fine particle paste, while the intensity of $CaCO_3$ was observed to be stronger than in cement paste, which is believed to be because more $CaCO_3$ was generated from old cement mortar or old cement paste. Fine particles included in recycled aggregate weremostly generated by abrasion between aggregates in the manufacturing process of recycled aggregate, and there may be few unhydrated cement particles or hydrated cement particles. The fine particles on the surface of aggregate may not directly affect the concrete strength, but $CaCO_3$ lowers the water absorption in concrete, which could have a positive impact on the workability with recycled concrete paste.

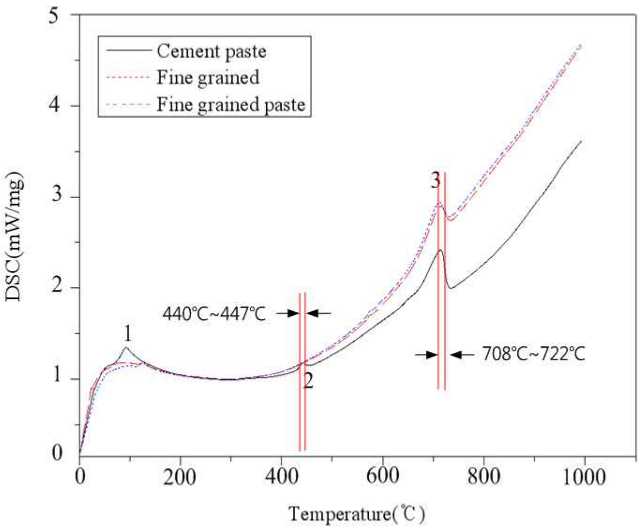

Figure 7. DSC curve of unhydrated fine-grained(curing ages 14 days)

4. Conclusion

1) Through DSC analysis, it was found that old mortar holds unhydrated cement particles, and could be hardened more firmly upon mixing with water.
2) Fine particles were generated through a reaction among silica powder (SiO_2), a component of sand, with $CaCO_3$, believed to be generated by combining $Ca(OH)_2$ with CO_2 in the air. Fine particles did not react with water, but silica powder(SiO_2) generated an alkali silicate gel in the reaction with alkali properties.

The old cement mortar attached on the surface of recycled aggregate could reduce the unit quantity when mixed into paste, and the initial strength can be slightly increased by the hydration reaction of unhydrated cement particles with water. However, a boundary is formed between the new mortar and old mortar or fine particles, which is believed to affect the adhesion strength between new and old mortar.

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