

EXAMINATION OF EVALUATION METHOD OF HYDRATION POTENTIAL OF DRY SLUDGE POWDER FOCUSING ON HYDRATION REACTION

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Abstract. *In recent years, dry sludge powder has attracted attention for reducing environmental impact as a method of reusing ready mixed concrete waste. Manufacturing process of the dry sludge powder is different from the ordinary portland cement. In the manufacturing process, there is drying process, and it is performed at high temperature. A characteristic of dry sludge powder is that it contains hydration products. However, few studies have focused on the effects of high temperature treatment and the hydration products contained in dry sludge powder. Therefore, in this study, we focused on the influence of hydration products contained in dry sludge powder and the high temperature treatment on hydration reaction. Firstly, we analyzed hydration products contained in the dry sludge powder. Next, the progress of hydration was examined by measuring the rate of heat of hydration. In addition, a sample was prepared by simulating the dry sludge powder process and it was treated at different temperatures and times. By examining this sample, the relationship between hydration product and hydration reaction was investigated. As a result, it was found that, as the amount of calcium hydroxide in the dry sludge powder decrease, the strength development becomes easier. Furthermore, the hydration potential of the dry sludge powder, can be derived by subtracting the ignition loss value of the raw dry sludge powder state from the measured ignition loss value.*

Keywords: *Dry sludge powder; Hydration product; Hydration potential formula; Strength development; Ignition loss;*

1. INTRODUCTION

In recent years, various efforts have been made to reduce environmental impact in many industries. In the ready-mixed concrete industry, along with CO₂ reduction, the reduction of residual concrete and return concrete is one of the major issues. Annually, about 1.5 to 2 million m³ of concrete are returned and it is expensive to dispose this material so it became a problem. Returned concrete is divided into aggregate and sludge water by the washing process. Figure 1 shows the washing process of the returned concrete. It is specified by the Japanese Industrial Standard (JIS) A 5308 for Ready-Mixed Concrete, that this washed aggregate can be reused as a collected aggregate. The supernatant water, that can be filtered and recovered from the sludge water, can also be reused as the mixing water of ready-mixed concrete. However, in the present situation, most of the material left after filtration of sludge water (sludge cake) is discarded as industrial waste. This disposal process is expensive and an economic burden for ready-mixed

concrete plants. Therefore, Ohkawa et al. have studied methods in which dry sludge powder (DSP), obtained by drying and crushing sludge cake, is used as a substitute for cement. Figure 1 shows the process of producing dry sludge fine powder. In the drying process, the burner is heated at about 300 to 500°C, and the inside of the rotary drum is processed at an actual temperature of about 100 to 200°C. Also, as shown in the figure, the time from when the water comes in contact with ready mixed concrete until the sludge cake is dried is referred to as the processing time. Returned concrete and leftover concrete are also washed immediately when they are returned to the ready-mixed concrete plant to collect aggregate. At this time, regarding to the dry crushing process, since the amount that can be processed at once by the drum-type burner to be dried is limited, there is also a time for stirring and storing in the state of sludge water. Therefore, there are DSP with different processing times. The difference in DSP processing time refers to the difference in time of agitation of the sludge water. Previous studies have reported that DSP has different density and specific surface area depending on the processing time. In addition, tests have been conducted to confirm strength and durability of structures using DSP. However, few studies have examined the relationship between hydration product, strength and the hydration reaction of the DSP, focusing on the correlation between the contained ingredients in the DSP raw powder. In this study, we investigated hydration reaction and hydration products from water contact of several DSPs with different processing times. In addition, in order to clarify the influence of hydration products contained in DSP on hydration reaction, the production process of DSP was simulated, and DSP samples were prepared and tested for different processing times and drying temperatures. The purpose of this study was to examine the relationship between these hydration-formed hydrates and the hydration reaction.

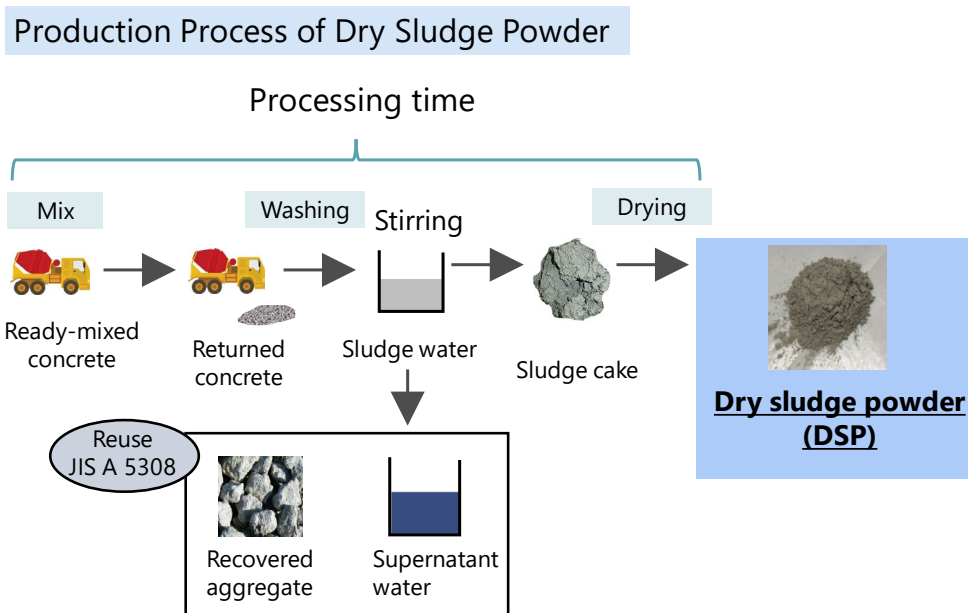


Figure 1. Process of Washing Method and Production Process of Dry Sludge Powder

Table 1 Details of DSP

DSP	OPC	DSP-A	DSP-B	DSP-C	DSP-D	DSP-E
Processing time (h)		8	5	9	24	12
Density (g/cm^3)	3.16	2.81	2.81	2.58	2.43	2.46
Specific surface area (cm^2/g)	3250	6020	7410	8920	10040	10590

Table 2 Details of hydrated cement

Hydrated cement	3h_40°C	24h_40°C	3h_105°C	24h_105°C	24h_300°C
Drying temperature (h)	3	24	3	24	24
Processing time (°C)	40		105		300

2. OUTLINE OF EXPERIMENT AND MATERIALS

2.1. Outline of Experiment

First, the hydration products contained in the raw powder were confirmed. During the processing time, the DSP is in contact with the water so it is considered that raw powder already contains hydration products because the hydration reaction is in progress. Hydration products contained in the raw powder were qualitatively analyzed by X-ray diffraction, and the quantitative analysis was performed by differential thermogravimetric analysis. At this time, in order to clarify the influence of the hydration products contained in the DSP on the hydration reaction, it was simulated the production process of the DSP and hydrated samples were produced with different processing times and the drying temperature. Thermogravimetric analysis was also performed.

Next, the influence of the hydration products contained in the raw powder submitted to the hydration reaction was examined. A cement paste was prepared, and powder X-ray diffraction was performed to confirm the hydrates formed as the hydration reaction proceeds. Differential thermogravimetric analysis was also performed to determine hydration products. Furthermore, the total hydration heat of cement paste was measured using a conduction calorimeter, and the progress of hydration reaction was confirmed. After that, mortar was made using DSP, and it was examined the relationship between strength and the degree of hydration progress of DSP affected mortar.

2.2. Material and mix proportion

For this study, it was used five kinds of DSP made with different processing times and prepared by simulating the method of making DSP and also ordinary portland cement (OPC) as reference. The details of each DSP and OPC are shown in Table 1, and for hydrated cement, it is shown in Table 2. The specific surface area, that is shown in Table 1, was measured using a braine permeation device. The processing time was chosen to be short and long, so that the differences in the progress of hydration between DSPs could be considered. The fine aggregate used in this study is a mountain sand from Kimitsu at Chiba Prefecture in Japan (Surface dry density: 2.62 g/cm³).

2.3. Cement paste specimen specification

The hydrated cement samples were made using a W/C factor of 200% with OPC cement paste mixed together using a stirrer devise. In this study, three hours and 24 hours were set as the processing time for mixing with the stirrer. After the predetermined time, the cement paste was dewatered with a suction funnel and dried using an electric furnace until the mass loss became constant at a set temperature. The drying temperature was set at 105°C, close to the actual drying temperature, and it was also used the 40°C and 300°C for comparison. After drying, the sample was ground using a grinding mill to obtain the DSP.

2.4. Mortar specimen mix proportion and compressive strength test

The mix proportion of mortar used in this research was 1 : 3 according to the cement strength test standard JIS R 5201. The size of the specimen was 40 × 40 × 160 mm. After demolding on the next day of placement, the samples were transferred to a constant temperature and humidity chamber (temperature 20 °C, humidity 60%) and subjected to sealed curing for 28 days. After curing was completed, a mortar compressive strength test was conducted in accordance with JIS R 5201.

2.5. Tests to consider hydration progress and hydration products

Measurement of the total hydration heat was performed to confirm the progress of hydration. The heat of hydration was measured over time using a conduction calorimeter. It is known that there is a correlation between the cement hydration speed and the total hydration heat. In this test, the binders OPC, DSP-B, DSP-C, and DSP-E were used. The cement paste used was W/C=55%. The specimens were weighed so the total amount of water and cement reach 4g, so after put together, they were mixed for 30 seconds. Following, a conduction calorimeter was installed, and hydration heat from immediately to 48 hours after water contact with material was measured at a constant temperature environment (20°C). X-ray diffraction was used to identify the hydration products contained. The raw powder of DSP, hydrated cement and OPC were analyzed. Differential thermogravimetric analysis was performed using TG-DTA for measurement at a heating rate of 20°C/min from 40°C to 1000°C under an N₂ flow environment. The amount of production was calculated from the TG curve by the dehydrated weight of the product from the inflection point of the DTA curve. The analysis was carried out using the DSP, the hydrated cement, and the raw powder of OPC as samples.

3. RESULT AND DISCUSSION

3.1. Hydration products of DSP and hydrated cement

Figure. 4 shows the results of powder X-ray diffraction of DSP raw material and hydrated cement. Unlike the other samples, the peak of ettringite was confirmed at 24 h_40 °C and 24 h_105 °C. The hydrates that can be identified in the raw powder are generally the same for any sample. However, focusing on the intensities of these peaks, different results were obtained depending on the powder. From this result, quantitative analysis of hydrate was performed.

The amount of hydration products contained in the raw powder of OPC, DSP and hydrated cement were measured, and the ratio was calculated. Figure 2 shows the content of calcium hydroxide and Figure 3 shows the content of calcium carbonate. DSP and hydrated cement are compared with OPC, and it turns out that both calcium hydroxide and calcium carbonate are contained. The amount of calcium hydroxide varie for DSP and hydrated cement. The longer the processing time, the more calcium hydroxide is contained. From this, it is considered that the calcium hydroxide contained in the sample is generated due to the progress of the hydration reaction during the water processing time. The amount of calcium carbonate contained in DSP was almost equal regardless of the processing time. Also, the hydrated cement contains less calcium carbonate than DSP. Calcium carbonate is derived from cement because the amount contained in the sample is equivalent to OPC. From this, it is thought that calcium carbonate contained in DSP is increased by the influence of fine particles derived from aggregate which could not be discharged by washing treatment and classification treatment. The samples that were stirred for 24 hours and dried at 40 °C decreased in the amount of calcium hydroxide and increased in the amount of calcium carbonate compared to the other samples stirred for 24 hours. This is due to carbonation of part of the sample during the drying process.

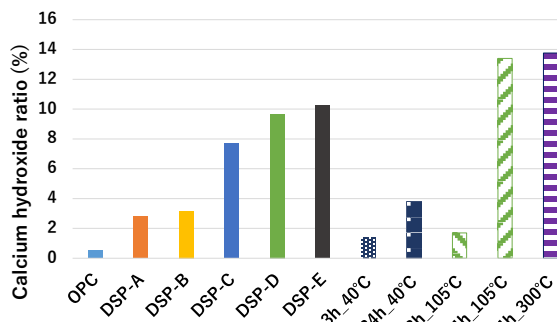


Figure 2 Calcium hydroxide content ratio

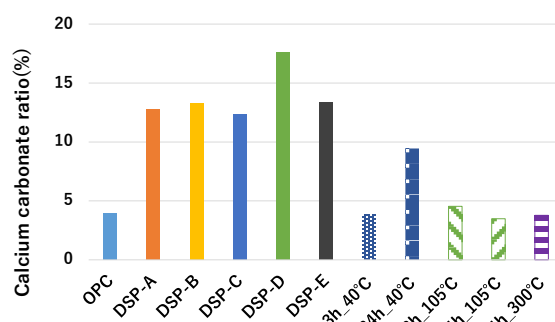


Figure 3 Calcium carbonate content ratio

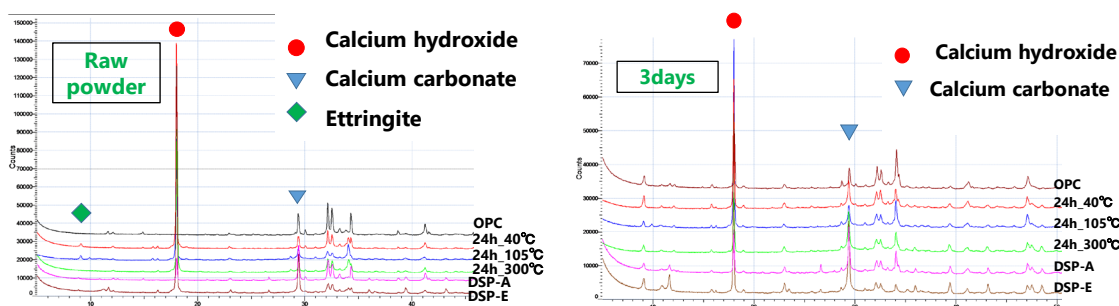
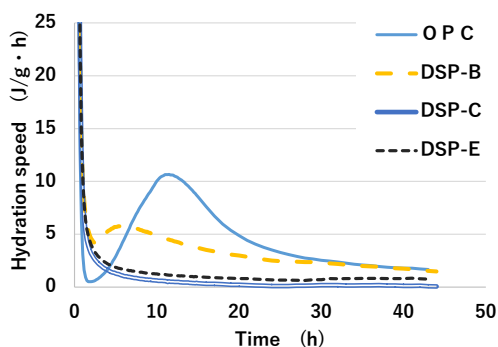


Figure 4 Hydration products content

3.2. Hydration progress and hydration products by DSP and hydrated cement

Figure. 4 shows the powder X-ray diffraction results of the 3 days old cement paste manufactured using DSP and the hydrated cement. The hydration products that could be confirmed were generally similar. However, in DSP, different peaks can be confirmed around $2\theta=10^\circ$. This was considered to require further study. Figure. 5 shows the results of total hydration heat measured with a conduction calorimeter. Figure 5 shows the results of total hydration heat amount. As shown in the figures, the shorter the DSP processing time, the larger the hydration reaction peak and the higher the integrated temperature. It is considered that this is due to the already developed hydration reaction affecting the processing time of DSP and hydrated cement. As the processing time is shorter, the hydration reaction does not progress within the processing time. Therefore, it is considered that there is a remaining capacity of hydration when water is put in contact with DSP and hydrated cement.



	24h	48h	
Total Hydration heat(J)	OPC	2837.4	3110.7
	DSP-B	1925.8	2181.8
	DSP-C	341.79	358.33
	DSP-E	708.3	792.53

Figure 5 Hydration speed of DSP

3.3. Consideration of DSP hydration

The results of making a cement paste using DSP and performing differential thermogravimetric analysis for each material age are shown. Figure 6 shows the progress of calcium hydroxide content. From this graph, the tendency of the transition of the amount of calcium hydroxide is divided into two. The calcium hydroxide content of the DSP exceeds the OPC in the raw powder state. After water contact, the OPC far exceeds the DSP and reverses. DSP-C, DSP-D, and DSP-E have the largest amount of calcium hydroxide in the raw powder state, and after contact with water, calcium hydroxide has decreased. The amount of calcium hydroxide in OPC, DSP-A and DSP-B increased with age. As the processing time of DSP-C, DSP-D, and DSP-E became longer, the amount of calcium hydroxide showed was smaller than the raw powder state. It can be seen that the DSP, with a short processing time, has a large amount of hydration products when compared to the DSP having a longer processing time.

3.4. Comparison of the hydration reaction of hydrated cement and DSP

Figure 7 shows the progress of calcium hydroxide ratio of hydrated cement and DSP, and Figure 8 shows the progress of calcium carbonate ratio. From the figures, it can be seen that the calcium hydroxide content of the hydrated cement, that was dried at 105°C and 300 °C, exceeds the DSP and is equivalent to the OPC. When the drying temperature was 40 °C the hydrated cement for 3 hours and 8 hours had calcium hydroxide equivalent to that of DSP-A. However, when the treatment time is 24 hours with drying temperature of 40 °C, almost no calcium hydroxide is produced below DSP-E. On the other hand, calcium carbonate is considered to not contribute to hydration because it hardly changed in proportion by 3 days of material age.

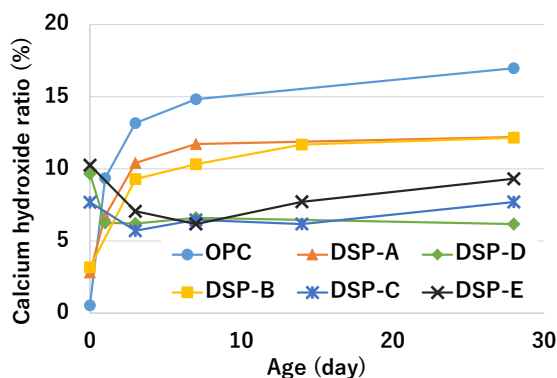


Figure 6 Calcium hydroxide content of DSP

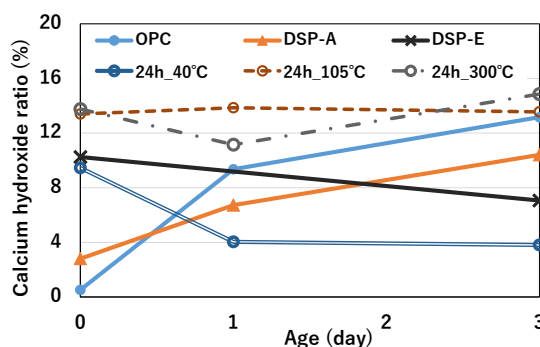


Figure 7 Calcium hydroxide content of hydrated cement

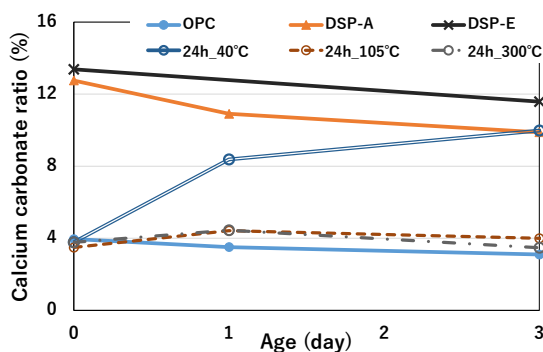


Figure 8 Amount of calcium carbonate

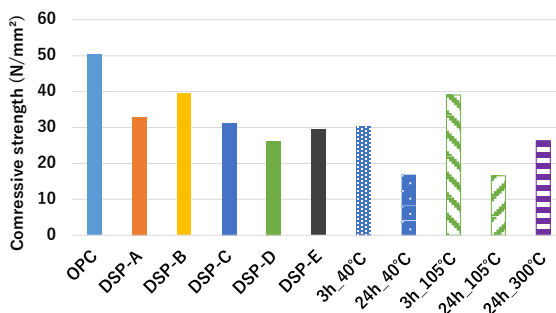


Figure 9 Compressive strength

3.5. Compressive strength of DSP

Compressive strength test was conducted to confirm the strength development of DSP. Figure 9 shows the compressive strength. The DSP and the hydrated cement do not reach the strength of the OPC. As in previous studies, samples with longer processing time had lower compressive strength development, and shorter processing times tended to increase it.

3.6. Consideration on the hydration potential of DSP

From the tendency of hydration of DSP, the evaluation method of strength expression of DSP is discussed. Generally, there is a correlation between strength and cement hydration and hydration products. However, DSP has a hydration product generated at the processing time. There is a problem that, even if ignition loss and calcium hydroxide amount are analyzed in order to measure the hydration reaction of DSP, it cannot be evaluated correctly. Therefore, the amount of hydrates that were generated during the processing time in the raw powder was subtracted from the amount of hydrate that was generated when the DSP got in contact with water. It was considered to use this as an evaluation of the hydration potential (%) of DSP. Therefore, the hydration potential was calculated as shown in the following equation (1). By subtracting the ig.loss value in the raw powder state from the ig.loss value at 3 days of age, we considered this value as capable of hydration reaction. Figure 10 shows the relationship between the calculated hydration potential and the compressive strength at 28 days. There was a correlation that the higher the hydration potential of DSP, the larger the compressive strength at 28 days of age, indicating the residual hydration ability of DSP. 24h_105°C and 24h_300°C showed large hydration potentials despite the large amount of calcium hydroxide. Compared with 24h_40°C, which was reacted for 24 hours and dried at 40°C, the hydration potential increased. This result suggests that the drying temperature of 105°C or more may affect the hydration reaction, and it is thought that further study is necessary in the future.

$$\text{Hydration potential} = \frac{3 \text{ days ig.Loss value} - \text{raw powder ig.Loss value}}{3 \text{ days ig.Loss value}} \quad (1)$$

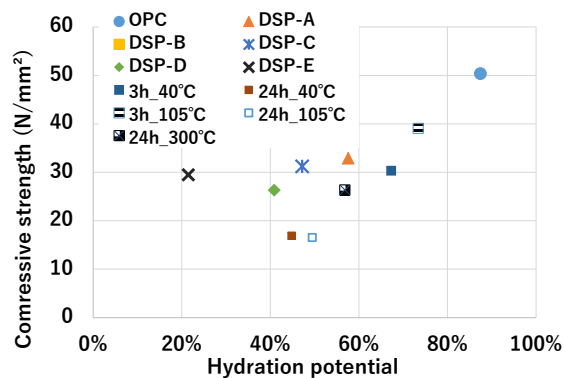


Figure 10 Relationship between compressive strength and hydration potential

4 CONCLUSIONS

- 1) The total hydration heat of DSP decreased as the treatment time increased. Also, the total hydration heat of DSP with short processing time was increased. This is the effect of the hydration reaction that has already progressed, because the degree of progression of hydration varies depending on the processing time of DSP.

- 2) The hydration potential of DSP can be calculated by subtracting the ignition loss value of the raw powder state of DSP from the measured ignition loss value.
- 3) Strength development can be evaluated by calculating hydration potential. By using this, it was shown that the smaller the amount of calcium hydroxide contained, the easier it is for strength to be developed.

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