Effects of Mixing Conditions and Increased Aluminate Phase on Slump Flow in High-Strength Concrete

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Abstract: An increase in construction projects using high-strength concrete is expected in Japan, necessitating corresponding advancements in manufacturing technologies. The fluidity of high-strength concrete can vary significantly depending on the mixing conditions, even when the mix design and environmental conditions are identical. Previous studies have focused on the initial dry mixing of fine aggregates containing surface water with cement and confirmed that this process can lead to differences in fluidity. In this study, we focused on the differences in cement components during the mixing process and examined their impact on fluidity. As a result, it was confirmed that the apparent specific surface area of the aluminate phase, which preferentially adsorbs admixture, decreased due to dry mixing, leading to differences in slump flow.

Keywords: High-strength concrete, dry mixing, admixture, pre-adsorption, aluminate phase

1.Introduction

Currently, Japan faces multiple societal challenges, such as how to achieve a low-carbon society, how to improve efficiency in response to a declining population, and how to efficiently transfer technical skills in an aging society.

The use of high-strength concrete is expected to increase, in response to the increasing frequency and severity of natural disasters, and based on policies such as disaster prevention, mitigation, and countermeasures against infrastructure deterioration aimed at strengthening national resilience. Furthermore, due to the nationwide population decline and shortage of workers in the construction industry, the use of precast concrete products is expected to increase as a means to shorten construction periods. Moreover, it is clearly stated in the purpose of the 2019 revision of JIS A 5308 that it aims to promote the use of high-strength concrete[1)].

Against this background, the use of high-strength concrete is expected to increase further, requiring not only construction techniques but also corresponding measures at batching plants. It is also known that mixing conditions affect the fluidity of concrete, with one contributing factor being the adsorption of admixtures onto cement particles[2)3)]. This effect is even more pronounced in high-strength concrete than in standard concrete due to its high cement content. However, few studies have attempted to clarify the extent and mechanisms of these effects in high-strength concrete mix designs. We believe that understanding the differences in fluidity associated with mixing conditions can contribute to the stable supply of high-strength concrete in the future.

Prior studies have reported that dry mixing (i.e., mixing fine aggregates containing surface water with cement at the initial stage) can cause variations in slump flow[2)3)]. It has also been reported that the slump flow variations caused by dry mixing during the mixing process are influenced by factors such as the flocculation of cement particles due to the hydration reaction between cement and surface water, and the residual amount of admixture in the liquid phase. However, since the specific surface area and chemical composition vary depending on the type of cement, it remains unclear whether the effect of dry mixing on slump flow is consistent across all types of cement.

In this study, multiple experiments were conducted using different types of cement to examine the effects of dry mixing on slump flow and the residual amount of admixture. In addition, focusing on surface water in fine aggregates and the admixture, both of which are identified as important indicators in previous studies, we further investigated the chemical aspects of admixture adsorption and discussed the process by which differences in slump flow arise due to dry mixing.

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2. Mixing Process in Previous Studies

Previous studies on mix designs for high-strength concrete have confirmed that performing dry mixing when using fine aggregates containing surface water results in an increase in slump flow[2)3)].

Furthermore, the increase in slump flow due to dry mixing is presumed to be caused by the flocculation of cement particles. **Figure 1** illustrates the currently assumed mixing process. The mechanism of improved fluidity through dry mixing, as assumed in this study, is explained in the following sequence.

A) Dry Mixing Stage

The surface water present on the fine aggregates initiates a hydration reaction with the cement particles. As the hydration begins, the cement particles become electrochemically unstable, leading them to aggregate in order to reach a more stable state. This aggregation results in the formation of flocs.

B) Mortar Mixing Stage

When water containing admixture is added to the mixture, the admixture is adsorbed (hereafter referred to as pre-adsorption) onto the surface of the flocs, while the residual admixture stays dissolved in the liquid phase.

C) Concrete Mixing Stage

Upon contact with the added coarse aggregates, the flocs disintegrate, exposing the surfaces of unhydrated cement particles.

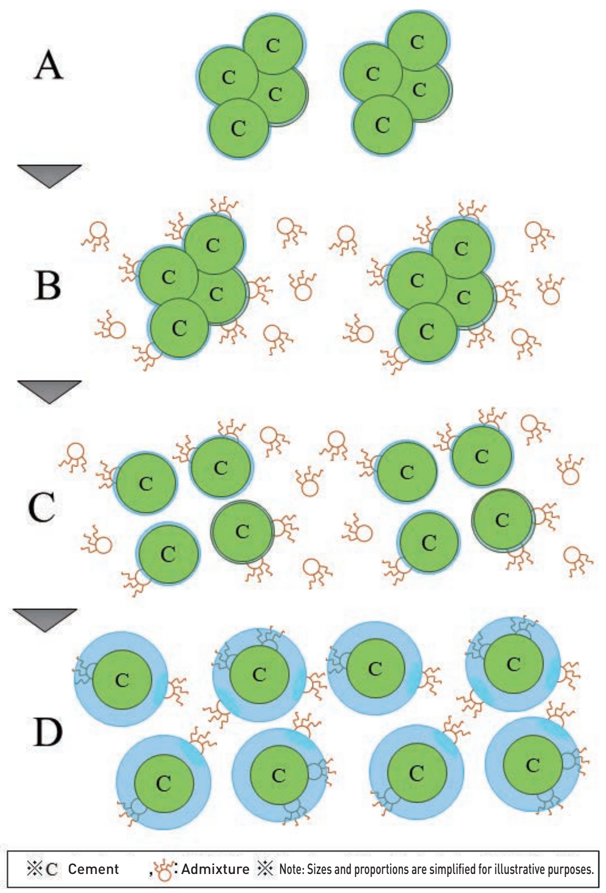


Figure 1: Assumed Mixing Process

Some exposure of adsorbed surfaces due to contact with fine aggregates already occurs at stage **B**. However, it becomes more pronounced at stage **C** due to the shear forces from the contact with the coarse aggregates.

D) Completion of Mixing

The residual admixture in the liquid phase is adsorbed onto the unhydrated cement surfaces exposed by the disintegration

Table 2 Materials

Materials	Type and Quality
Fine Aggregate *S*	Crushed sand Rock type: Andesite Air-dried density: 2.54 g/cm^3
Coarse Aggregate *G*	Crushed stone Rock type: Andesite Air-dried density: 2.67 g/cm^3
Admixture *Pc*	High-range water-reducing admixture Main component: Polycarboxylate-based compound

Table 1 Mix Design of High-Strength Concrete (80-60-20L)

Maximum size of coarse aggregate (mm)	Slump flow (cm)	Water-cement ratio (%)	Air content (%)	Fine aggregate ratio (%)	Unit content (kg/m^3)				
					Water *W*	Cement *C*	Fine aggregate *S*	Coarse aggregate *G*	Admixture *Pc*
20	60.0	21.4	2.0	44.4	175	818	650	815	8.18

of the flocs (hereafter referred to as post-adsorption).

To maintain fluidity after mixing, a sufficient amount of admixture must remain at stage **D**. An excess amount must also be available for new adsorption onto the unhydrated cement surfaces during post-adsorption. Additionally, the longer the dry mixing time, the more the cement particles aggregate. This results in a smaller specific surface area of the flocs formed at stage **A**. Therefore, with longer dry mixing, less admixture is consumed through pre-adsorption at stage **B**. This leaves more admixture available for post-adsorption at stage **D**, which leads to an increase in slump flow (hereafter referred to as the dry mixing effect[2]).

However, as mentioned in **Chapter 1**, the current mixing process does not account for differences arising from factors such as the specific surface area or composition of the cement. Therefore, these aspects are examined in the following chapters.

3. Experimental Overview

3.1 Materials

Table 1 shows an example of the high-strength concrete mix with a design compressive strength of 80 N/mm^2 used in this study. The admixture dosage for each test day was set based on the results of preliminary tests conducted with the concrete mix, and the mixture was adjusted accordingly. The materials used are shown in **Table 2**. Four types of cement were used: low-heat cement **(L)**, moderate-heat cement **(M)**, ordinary Portland cement **(N)**, and high-early-strength cement **(H)**. The chemical compositions and specific surface areas of each cement are shown in **Table 3**. The admixture was added in proportion to the unit weight of cement. Since the dry mixing effect is considered to be caused by the interaction between the surface water on the fine aggregate and the cement particles, the surface water content of the fine aggregate was standardized to **3%** in this study, following previous studies[2)3)].

3.2 Mixing Procedure

A twin-shaft forced mixer with a capacity of **60 liters** was used for mixing, and the mixing volume was set to **36 liters**. **Figure 2** shows the mixing procedure. The total mixing time was **10 minutes**: **7 minutes** for mortar mixing with fine aggregate, cement, water, and admixture, and **3 minutes** for concrete mixing after adding coarse aggregate. After mortar mixing, the mortar flow was measured, and after concrete mixing, the slump flow was measured. For each mixing process, the dry mixing time was set to one of **0 seconds, 30 seconds, or 90 seconds.** It should be noted that since the dry mixing time was included in the mortar mixing time, the total mixing time remained unchanged. All tests were conducted indoors under controlled conditions with a temperature of **20 ± 2°C** and humidity of **50%** or higher.

3.3 Measurement of Residual Amount of Admixture

In **Chapter 5**, the residual amount of admixture in the mortar samples was measured after stage **B in Figure 1** (i.e., before the addition of coarse aggregate). The measurement involved separating the mortar samples into liquid and solid phases using a centrifuge. The extracted liquid phase was then analyzed by thermal analysis **(TG/DTA)**, and the residual amount of admixture in the liquid phase was calculated based on the weight change within the temperature range where the active components of the admixture combust. The measurement was performed six times, and the average values were compared.

4. Effect of Cement Type on Dry Mixing Effect

In the previous study presented in **Chapter 2**, the focus was placed on the physical properties of cement particles, and the process by which dry mixing improves fluidity was described in terms of the reduction in specific surface area due to floc formation. This chapter presents the experiments conducted to investigate how the type of cement, in terms of chemical properties, affects the dry mixing effect. The materials and mixing procedure followed the experimental conditions described in the previous section.

4.1 Effect of Cement Specific Surface Area

(1) Overview of the Experiment

Using four types of cement with different specific surface areas (**L, M, N,** and **H**), the relationship between slump flow and specific surface area was examined.

Table 3 Chemical Composition and Specific Surface Area of Each Cement

Type of Cement	Chemical Composition (%)				Specific Surface Area (cm²/g)
	C_3S	C_2S	C_3A	C_4AF	
Low-heat Portland Cement (L)	27	55	2	9	3130
Moderate heat Portland Cement (M)	43	36	4	13	3120
Ordinary Portland Cement (N)	56	18	9	9	3320
Rapid hardening Portland Cement (H)	63	12	9	8	4350

To isolate the effect of cement specific surface area, the admixture dosage was fixed at **0.65%** and the dry mixing time at **30 seconds**. The total volume varied due to differences in the density of each cement type. However, volume variations were not considered for **L, M,** and **N,** as the impact was assumed to be negligible.

(2) Results and Discussion

Figure 3 shows the slump flow results for each type of cement. Although the low-heat cement **(L)**, moderate-heat cement **(M)**, and ordinary Portland cement **(N)** have similar specific surface areas, their slump flows differed significantly. Taking low-heat cement **(L)** as the reference, the slump flow of the moderate-heat cement **(M)** was 23.0 cm lower than that of the low-heat cement **(L)**, and for ordinary cement **(N)**, the slump flow could not be measured, and only slump of 6 cm was observed. Despite having similar specific surface areas, the large differences in flow suggest that cement composition also has a significant influence.

Additionally, the high-early-strength cement **(H)** has a specific surface area approximately **1000 cm²/g** larger than the other cements. It is believed that more admixture was consumed during pre-adsorption due to the larger surface area, leaving insufficient admixture for post-adsorption and resulting in no slump flow being observed.

4.2 Effect of Cement Composition

(1) Overview of the Experiment

In Section **4.1**, it was observed that slump flow varied significantly even among cements with similar specific surface areas. This suggests that fluidity is also influenced by the chemical composition of the cement. Therefore, the relationship between slump flow and the cement composition for each type of cement was examined.

(2) Results and Discussion

Among the cement components, an approximate correlation was observed between the content of tricalcium aluminate (hereafter, **C_3A**) and slump flow. Accordingly, the relationship between slump flow and **C_3A** content is shown in **Figure 4**. For cements with similar specific surface areas—namely low-heat, moderate-heat, and ordinary Portland cement—the **C_3A** content increased in the order of low-heat cement **(L)** < moderate-heat cement **(M)** < ordinary cement **(N)**, while the slump flow decreased in the order of low-heat cement**(L)** > moderate-heat cement **(M)** > ordinary cement

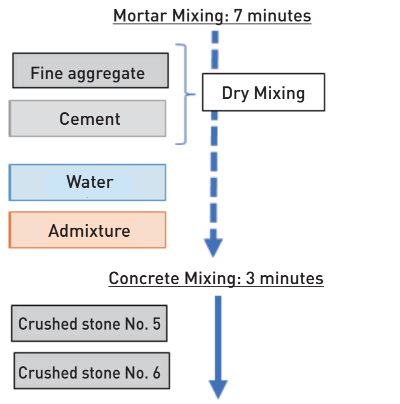


Figure 2: Mixing Procedure

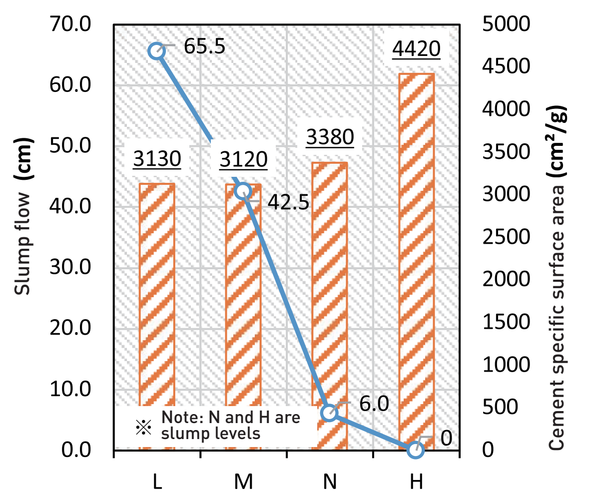


Figure 3: Slump Flow and Cement Specific Surface Area

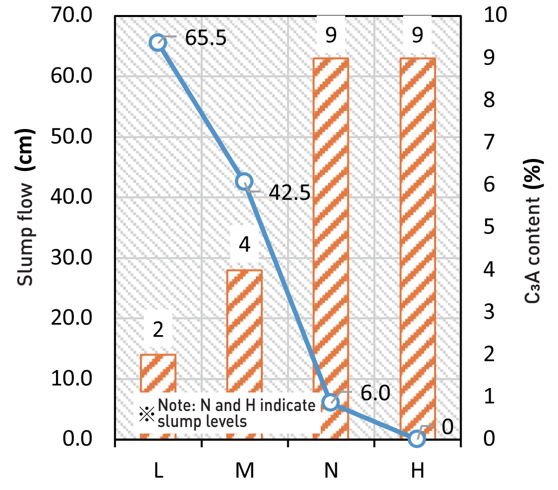


Figure 4: Slump Flow and C_3A Content

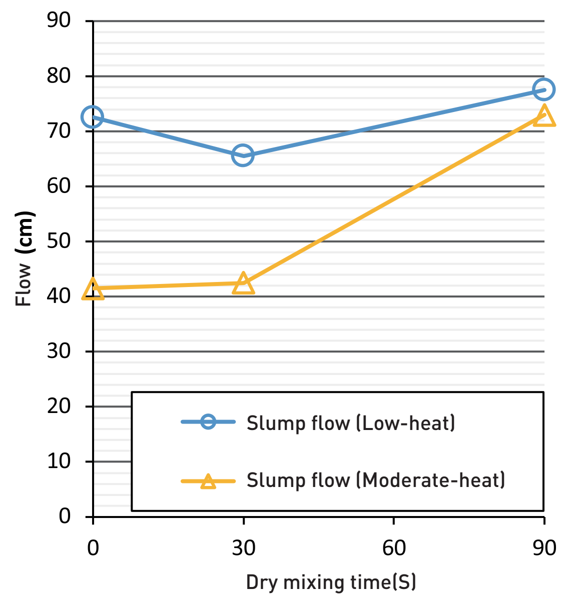


Figure 5: Dry Mixing Time and Slump Flow

(N). This confirms that slump flow decreases as the C_3A content increases. The pre-adsorption of admixture due to the initial hydration of C_3A is a potential reason for the reduced slump flow in cements with high C_3A content[4)5)6)]. Since the admixture is preferentially adsorbed onto C_3A, cements with higher C_3A content exhibit increased pre-adsorption at **stage B in Figure 1**, resulting in a lower residual amount of admixture in the liquid phase. The amount of admixture available for post-adsorption at **stage D in Figure 1** is reduced. Consequently, the residual amount of admixture at the end of mixing becomes insufficient, thereby reducing the slump flow. Therefore, differences in slump flow can be attributed to factors beyond specific surface area, even when the values are similar.

4.3 Influence of Cement Type on Dry Mixing Effect

(1) Overview of the Experiment

In **Sections 4.1** and **4.2**, it was confirmed that the slump flow of various cements is significantly affected by the C_3A content. Based on this, it was assumed that the dry mixing effect also varies depending on the C_3A content. Therefore, the influence of dry mixing time was examined under different C_3A content conditions. Low-heat cement and moderate-heat cement were selected for the experiment, as slump flow measurements were possible when a fixed amount of admixture was added to these cements.

(2) Results and Discussion

Figure 5 shows the relationship between dry mixing time and slump flow. For both low-heat cement and moderate-heat cement, the maximum slump flow was observed at a dry mixing time of **90 seconds**. Even with cements with different C_3A contents, an increase in slump flow with longer dry mixing time was confirmed.

Additionally, at dry mixing times of **0 seconds** and **30 seconds**, a difference in slump flow of **20 to 30 cm** was observed between the low-heat cement and moderate-heat cement. In contrast, at a dry mixing time of **90 seconds**, there was almost no difference in slump flow between the two cements. Since the rate of increase in slump flow with dry mixing time differed between the cements with similar specific surface areas, it is presumed that dry mixing caused differences in the amount of admixture adsorbed onto C_3A.

Since the C_3A content is lower in the low-heat cement than in the moderate-heat cement, it is considered that in cases of short dry mixing times (**0 seconds** and **30 seconds**), the amount of admixture pre-adsorbed as shown in **Figure 1B** was lower for the low-heat cement than for the moderate-heat cement. As a result, the amount of admixture available for post-adsorption in **Figure 1D** was insufficient for the moderate-heat cement, leading to a smaller slump flow compared to the low-heat cement. On the other hand, in cases of long dry mixing times **(90s)**, it is inferred that the apparent specific surface area available for C_3A adsorption decreased due to floc formation shown in **Figure 1A**. Consequently, the amount of admixture pre-adsorbed as shown in **Figure 1B** decreased, and as shown in **Figure 1D**, enough admixture remained for post-adsorption in both the low-heat and moderate-heat cements, resulting in similar slump flow values.

5. Effect of Increased Aluminate Phase on Slump Flow

(1) Overview of the Experiment

In **Chapter 4**, it was confirmed that the effect of dry mixing varied depending on the type of cement. It was also inferred that prolonged dry mixing could reduce the amount of admixture pre-adsorbed onto C_3A. However, since the types of cement differed, the influence of components other than C_3A could not be excluded. Therefore, in this chapter, in order to focus solely on C_3A, onto which admixture is preferentially adsorbed, an experiment was conducted by partially replacing the low-heat cement with aluminum oxide powder (hereinafter referred to as alumina powder). The replacement ratio of alumina powder to low-heat cement was set at **1% by weight of cement.** The comparison was made using the following **three** patterns:

1.Dry mixing for **30s**
2.Dry mixing for **30s** (with **1%** alumina)
3.Dry mixing for **90s** (with **1%** alumina)

The materials and mixing procedures were the same as those described in **Chapter 4**. In addition, since the replacement ratio was only **1%**, its effect on the specific surface area was considered negligible, and differences in specific surface area after replacement were not taken into account.

(2) Results and Discussion

Figure 6 presents the slump flow for each pattern, and **Figure 7** presents the corresponding residual amount of admixture. In **Figure 6**, a decrease in slump flow is observed when comparing **30-second** dry mixing with and without **1%** alumina. **Figure 7** similarly shows a decrease in the residual amount of admixture. Since the residual admixture was measured after the stage shown in **Figure 1B** (before the coarse aggregate was added), it can be inferred that the increase in alumina powder led to an increase in the amount of admixture pre-adsorbed, which in turn reduced the amount available for post-adsorption and resulted in a lower slump flow.

In addition, when comparing the **30-second** dry mixing with **1%** alumina and the **90-second** dry mixing with**1%** alumina, an increase in slump flow was observed with the longer dry mixing time. Since the residual amount of admixture also increased with longer dry mixing, it can be inferred that dry mixing decreased the admixture pre-adsorption onto alumina. In other words, with longer dry mixing time, the flocs formed by cement particles likely reduced the specific surface area of the alumina powder (see **Figure 1A**), leading to a decrease in admixture pre-adsorption.

Compared to **30-second** dry mixing, the **90-second** dry mixing with **1%** alumina resulted in higher slump flow and a greater residual amount of admixture. Therefore, the increase in slump flow due to **90 seconds** of dry mixing outweighed the reduction caused by admixture pre-adsorption onto **1%** alumina.

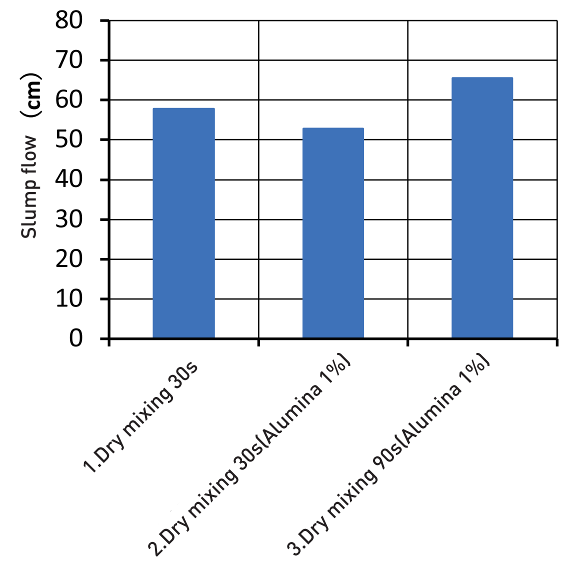


Figure 6: Dry Mixing Time and Flow

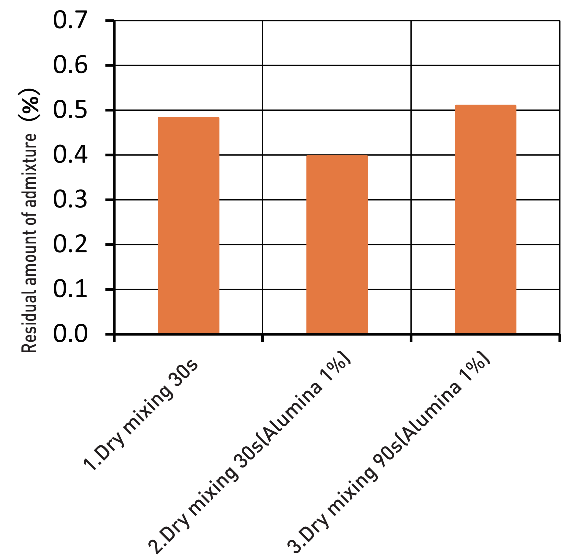


Figure 7: Dry Mixing Time and Residual Amount of Admixture

6. Mixing Process Inferred from Experimental Results

Figure 8 illustrates the mixing process that takes into account both the dry mixing time and the effects of cement components discussed in **Chapters 4 and 5**. Based on the present study, the mechanism of improved fluidity through dry mixing can be explained in the following sequence.

A) Dry Mixing Stage

The surface water present on the fine aggregates initiates a hydration reaction with the cement particles. As the hydration begins, the cement particles become electrochemically unstable, leading them to aggregate in order to reach a more stable state. This aggregation results in the formation of flocs. It is inferred that the flocs grow larger with longer dry mixing time, leading to a reduction in the specific surface area of cement (especially **C_3A**) available for admixture adsorption.

B) Mortar Mixing Stage

When the admixture is added, it adsorbs onto the surface of the flocs, preferentially onto **C_3A**.

C) Concrete Mixing Stage

Through mixing with the added coarse aggregate, the flocs break apart.

D) After Completion of Mixing

The residual admixture in the liquid phase is adsorbed onto the unhydrated cement surfaces exposed by the disintegration of the flocs.

In the mixing process in **Figure 1**, it was previously inferred that the effect of dry mixing leads to an increase in slump flow due to a reduction in the floc's specific surface area caused by the formation of cement particle flocs at stage **A**, and a decrease in the amount of admixture adsorbed in advance at stage **B**, resulting in a greater amount of admixture available for post-adsorption at stage **D**.

However, the present study focused on cement components and confirmed that even when the specific surface area of the cement is the same, the amount of residual admixture varies depending on the **C_3A** content. Therefore, it was inferred that dry mixing causes the **C_3A** specific surface area to decrease due to floc formation at stage **A**, and that the amount of admixture preferentially adsorbed onto **C_3A** at stage **B** is reduced, which in turn increased the amount of admixture available for post-adsorption at stage **D**, resulting in increased slump flow.

Accordingly, the following two main factors can be considered to contribute to the increase in slump flow due to dry mixing: the reduction in surface area available for admixture adsorption caused by floc formation of cement particles; and the apparent decrease in the **C_3A** specific surface area, which reduces the amount of admixture adsorbed in advance.

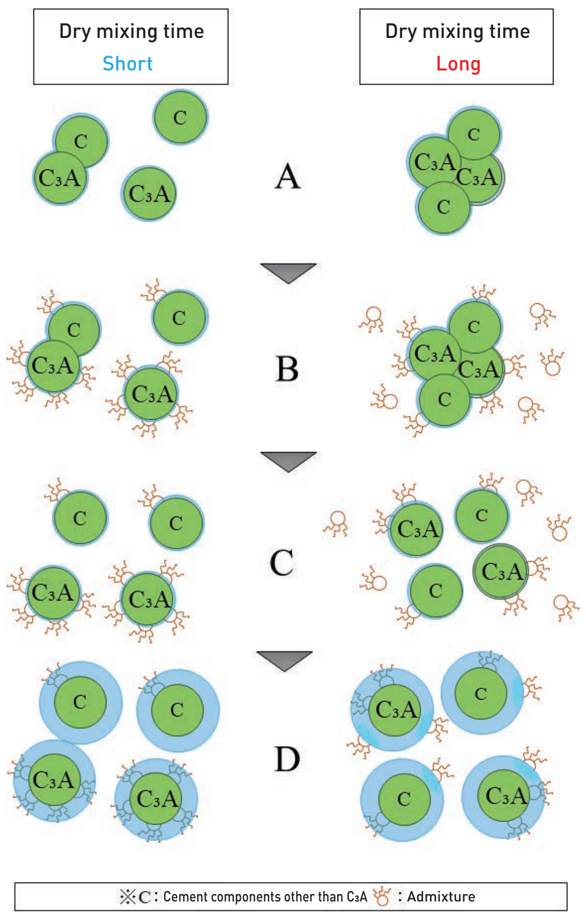


Figure 8: Mixing Process Inferred from This Study

7.Conclusion

The findings obtained in this study are summarized as follows:

(1) For the mix designs used in this study, an increase in slump flow with longer dry mixing time was confirmed for all types of cement: low-heat cement, moderate-heat cement, and alumina-substituted low-heat cement.

(2) Even when dry mixing time was constant and the specific surface area of cement was similar, slump flow differed depending on the cement composition. This difference was attributed to the amount of admixture preferentially adsorbed onto **C_3A**. With longer dry mixing time, sufficient admixture remained for post-adsorption even in cements with different compositions, resulting in similar slump flow.

(3) It was inferred that two mechanisms contribute to the increase in slump flow: (1) a reduction in the specific surface area of cement particles, which decreases admixture adsorption, and (2) a reduction in the amount of admixture preferentially adsorbed onto **C_3A**. These mechanisms allowed more admixture to remain for post-adsorption.

These results were obtained using high-strength concrete mix designs in this study. Going forward, further detailed investigation will be conducted to determine whether similar results can be obtained with other high-strength concrete mix designs and with normal concrete, in order to evaluate the general applicability of the mixing process inferred in this study.

References

1) JIS A 5308:2019. (2019). Ready-Mixed Concrete.

2) Sakamoto, Y., Kawasaki, Y., Fukuyama, T., & Kim, Y. (2022). Influence of Dry- Mixing on Mortar Flow for High-Strength Concrete. Proceedings of the Japan Concrete Institute, 44(1), 850–855.

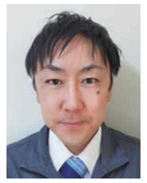
3) Sakamoto, Y., Kawasaki, Y., Fukuyama, T., & Kim, Y. (2023). Effect on the Slump Flow of High-Strength Concrete Caused by Floc Formation during Dry-Mixing. Proceedings of the Japan Concrete Institute, 45(1), 826–831.

4) Maruya, E., Ichinose, R., & Sakai, E. (2010). Fluidity and Hydration Characteristics of Aluminate-Rich Cement with Added Admixture. Cement Science and Concrete Technology, (64), 53–60.

5) Nakaguchi, A., Mori, T., Matsuzawa, K., & Kurokawa, D. (2019). Design and development of cement with increased minor additional constituents and aluminate phase—Part 1: Quality Evaluation of Cement. Cement Science and Concrete Technology, 73(1), 429–435.

6) Ohta, A., & Uomoto, K. (1999). A Study of the Dispersing Effects of Polycarboxylate-Based Dispersant on Fine Powder Particles. Journal of the Japan Concrete Institute, 10(2), 131–136.

Author



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