Consideration of the Effects of Polyvalent Cations in Mixing Water on the Fluidity of Concrete

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ABSTRACT

This study investigates the effects of polyvalent cations (mainly Ca^{2+} and Mg^{2+}) contained in mixing water on the fluidity of fresh concrete. The fluidity of mortar and concrete was evaluated using mixing water with different concentrations of polyvalent cations. The results showed that, in normal-strength concrete mixtures, the influence of polyvalent cations on the fluidity was small, whereas in high-strength concrete mixtures, the presence of polyvalent cations reduced fluidity. Chemical analyses revealed that a large amount of unadsorbed admixture remained in the liquid phase of mortar with reduced fluidity, suggesting a mechanism by which the dispersibility of cement particles is hindered. The influence of polyvalent cations was found to be more evident in high-powder-content mixtures where the dispersing effect of admixtures is significant.

Keywords: polyvalent cations; polycarboxylate-based admixture; fluidity; high-strength concrete; cross-linking; thermal analysis

1. Introduction

Concrete is an indispensable construction material widely used in various infrastructure systems in modern society, and its performance is required to satisfy multiple demands such as durability, safety, and constructability. Among these, the properties of fresh concrete during the construction stage are extremely important, as they are directly related to the ease of placement and compaction, crack resistance, and ultimately the quality of the hardened concrete. Therefore, appropriate control of fresh concrete properties is a fundamental and practical issue in concrete engineering.

In particular, fluidity is a key property that directly affects the workability of concrete. Fluidity is primarily governed by the viscosity of the cement paste, the shape and proportioning of aggregates, and the type and dosage of admixtures. In addition, the quality of mixing water is also an important factor that influences concrete fluidity.

In actual production environments, the quality of mixing water varies widely by region, ranging from soft water to hard water, and such water sources are commonly used¹⁾. However, practical standards generally assume potable water and specify only minimum requirements, and systematic evaluations of the effects of water quality on fluidity remain insufficient. In response to these issues, from the perspective of recent SDGs, mixture design that accounts for regional water quality is expected to contribute to both the rational use of high-range water-reducing admixtures and labor savings through stabilized placement of high-strength concrete members.

Previous studies have shown that the addition of finely powdered calcium hydroxide can lead to enhanced strength development²⁾. It has been reported that when a large amount of Ca^{2+} is added to the mixing water, Ca^{2+} forms bridges between the negatively charged silica surface and the carboxyl groups of polycarboxylate, resulting in a significant change in the fluidity of fresh concrete due to adsorption of the polycarboxylate-based admixture³⁾. These findings suggest that ions such as Ca^{2+}, collectively referred to as polyvalent cations, may influence not only the early development of strength by accelerating the hydration reactions of cement, but also the fluidity of fresh concrete by governing the formation of flocculated structures and the state of dispersion. However, most previous studies have focused primarily on strength evaluation or on the fluidity under a single mixture design. Systematic data on the effects of polyvalent cations on the fluidity across different mixture designs remain limited.

This study aims to systematically evaluate the effects of mixing water with different concentrations of polyvalent cations on the fluidity of fresh concrete in various mixture designs, including normal-strength and high-strength concretes, and to clarify changes in fluid characteristics arising from differences in water quality. Accordingly, the findings are expected to help reduce variability in workability under different water quality conditions and to contribute to the establishment of guidelines for optimal selection of mixing water and construction management. In addition, this study provides important insights into the development of high-performance concrete tailored to regional water quality and the stabilization of on-site construction practices.

In this paper, the fresh concrete fluidity obtained using different mixing waters was compared by employing a 5-L Hobart mixer and a 60-L twin-shaft forced mixer. The effects of polyvalent cations, particularly Ca^{2+} and Mg^{2+}, in the mixing waters on the mixing behavior of mortar and concrete were examined. Furthermore, the adsorption behavior of admixtures was investigated by measuring the residual admixture ratio, and an attempt was made to elucidate the mechanisms by which ion concentrations affect particle dispersion. These investigations were aimed at understanding changes in the properties of fresh concrete under differing water quality conditions and obtaining fundamental knowledge that contributes to the appropriate use of mixing water according to regional conditions, the selection of admixtures, and construction management.

2. Materials and Mix Proportions

This section presents an overview applicable to all experiments described in this paper. A list of the materials used in the experiments is shown in **Table 1**. It should be noted that the surface moisture content of the fine and coarse aggregates was adjusted to 3.5% and 0.5%, respectively, prior to use.

The concretes investigated consisted of two types: a normal-strength concrete mix with a specified design compressive strength of 24 N/mm² and a high-strength

Table 1: Materials used

Material	Type and Quality
Mixing Water *Ws*	Soft water Tap water from Akashi City, Hyogo Prefecture, softened by ion exchange
Mixing Water *Wh*	Hard water Mineral water (France)
Cement *CN*	Ordinary Portland cement Density: 3.16 g/cm³
Cement *CL*	Low-heat Portland cement Density: 3.23 g/cm³
Fine Aggregate *S*	Crushed sand (Rock type: Andesite) Saturated surface-dry (SSD) density: 2.54 g/cm³, Water absorption: 1.65% Source: Nishijima, Ieshima-cho, Himeji City, Hyogo Prefecture
Coarse Aggregate *G*	Crushed stone (Rock type: Andesite) Saturated surface-dry (SSD) density: 2.67 g/cm³, Water absorption: 0.96% Source: Osawa, Shikata-cho, Kakogawa City, Hyogo Prefecture
Admixture *SP1*	AE water-reducing admixture Main components: a composite of lignin sulfonate compounds and polycarboxylate ether
Admixture *SP2*	High-range water-reducing admixture Main component: a polycarboxylate-based compound

Table 2: Normal-strength concrete mix proportion

Water–cement ratio (%)	Fine aggregate ratio (%)	Bulk volume of coarse aggregate (m³/m³)	Unit quantity (kg/m³)				
			Water (*Ws*, *Wh*)	Cement (*CN*)	Fine aggregate (*S*)	Coarse aggregate (*G*)	Admixture (*SP1*)
57.2	48.8	0.581	187	327	820	905	Adjustment value

Table 3: High-strength concrete mix proportion

Water–cement ratio (%)	Fine aggregate ratio (%)	Bulk volume of coarse aggregate (m³/m³)	Unit quantity (kg/m³)				
			Water (*Ws*, *Wh*)	Cement (*CN*)	Fine aggregate (*S*)	Coarse aggregate (*G*)	Admixture (*SP1*)
21.4	45.6	0.522	175	818	650	815	Adjustment value

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concrete mix with a specified design compressive strength of 80 N/mm^2. The respective mix proportions are shown in **Tables 2** and **3**.

Both *SP1* and *SP2* are admixtures containing compounds with carboxyl groups as functional groups; however, *SP1* exhibits superior flow-retention performance, whereas *SP2* is superior in terms of initial fluidity development.

The admixtures were added in proportion to the unit cement content. The dosage was determined on the day of testing by adjusting the mix proportions based on preliminary mixing tests conducted using mortar and concrete for each mix.

All experiments were conducted indoors at a temperature of 20 ± 2°C and a relative humidity of 60% or higher.

3. Analysis Results of Mixing Waters

In this study, two types of mixing water (*Ws* and *Wh*) were prepared to evaluate the effects of the concentration of polyvalent cations in mixing water on fluidity. This section presents the analysis results for each type of mixing water. The surface moisture of the fine and coarse aggregates was excluded from the analysis because the contribution was negligible.

Two types of analyses—elemental analysis and pH testing—were conducted for the mixing water. Elemental analysis was performed using inductively coupled plasma optical emission spectrometry (ICP-OES) and atomic absorption spectrometry (AAS). It is difficult to obtain accurate values for Na and K using ICP-OES, and therefore, these elements were additionally measured by AAS for complementary evaluation. The target elements included four major cations commonly present in water, that is, Ca, Mg, Na, and K, as well as Al, Si, and Fe, which are contained in the cement, for a total of seven elements. In addition, pH testing was conducted using the glass electrode method (GE) with a pH meter to assess the alkalinity of the mixing waters.

The results of the elemental analysis and pH testing are summarized in **Table 4**.

When referring to the amounts of elements as analysis values, elemental symbols (e.g., Na, Ca) are used, whereas ionic symbols (e.g., Na^{+}, Ca^{2+}) are used when indicating chemical species present in solution. In general, alkali metals and alkaline earth metals such as Na, K, Ca, and Mg are present almost entirely in ionized form in aqueous solutions near a neutral pH.

Based on the concentrations of Ca and Mg calculated from the elemental analysis results, the water hardness was determined to be 0.6 mg/L for Ws and 1475 mg/L for *Wh*. According to the U.S. Geological Survey (USGS), *Ws* is classified as soft water, whereas *Wh* is classified as very hard water4).

During the water-softening process applied to *Ws*, Ca^{2+} and Mg^{2+} contained in potable water were replaced with Na^{+}. As a result, the Na concentration in *Ws* increased relative to that of the original potable water and exhibited a higher value than that of *Wh*. A previous study5), however, reported that when mixing water with approximately a 1000-fold difference in Na^{+} concentration was used, the resulting difference in flow value was on the order of 1–10 cm. In the present study, the difference in Na concentration between the mixing waters was approximately one order of magnitude. Therefore, the influence of differences in Na concentration in this study is considered to be small.

It should be noted that the difference in pH between the two mixing waters was 0.39. A previous study6) has shown that differences in pH values of 1.5 and 7 can affect fluidity; however, the pH range of the mixing waters examined in this study was extremely narrow compared with that in the previous research. Accordingly, the influence of pH on the fluidity in this study is considered to be small.

Table 4: Analysis results of mixing water

	Element concentrations (mg/L)							pH value
	Na	K	Mg	Ca	Al	Si	Fe	
Ws	90	0.2	0.03	0.18	0.03	6.6	<0.01	7.85
Wh	9.4	3.0	67	480	<0.01	4.5	<0.01	7.26
Measurement method	AAS		ICP-OES					GE

4. Effect of Hobart Mixer on Mortar

In this section, based on the differences in the amounts of polyvalent cations in the mixing water determined by elemental analysis, the effects of mixing water on the fluidity of mortar mixed using a Hobart mixer are investigated.

4.1 Experimental Overview

A Hobart mixer with a 5-L mixing capacity was used, and tests were conducted using various concrete mix designs with two types of mixing water. The quantities of each material were calculated on a per-liter basis from the specified mix proportions shown in **Tables 2** and **3**, and mortar was prepared and mixed accordingly. The mixing procedures for the normal-strength and high-strength concrete mixtures are shown in **Figure 1**. After the mixing procedures were completed, the mixed mortar was placed into the flow cone specified in JIS R 5201, and the flow cone was then lifted to measure the mortar flow.

4.2 Mortar Flow of Normal-Strength Concrete Mixtures

Figure 2 shows the mortar flow values obtained with each type of mixing water. When *Ws* and *Wh* were used as the mixing water, the difference in the mortar flow values was 0.5 cm.

4.3 Mortar Flow of High-Strength Concrete Mixtures

Figure 3 shows the mortar flow values obtained using each type of mixing water. When *Ws* and *Wh* were used as the mixing water, the difference in the mortar flow values was 1.5 cm. When a Hobart mixer was used for mixing, the small mixing capacity made it difficult to clearly identify changes in fluidity attributable to differences in mixing water. However, the observation of a slight difference in the flow values suggests that the type of mixing water may influence the fluidity of the mortar.

In the next section, to verify the effects under conditions closer to actual construction practice, the influence of mixing water will be clarified using concrete containing coarse aggregate rather than a small amount of mortar alone.

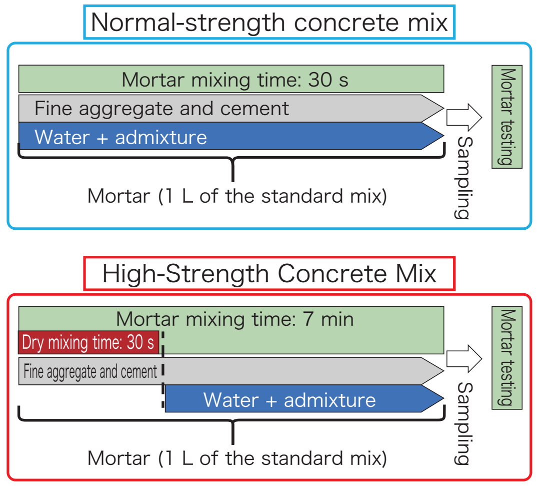


Figure 1: Mixing procedure using a Hobart Mixer

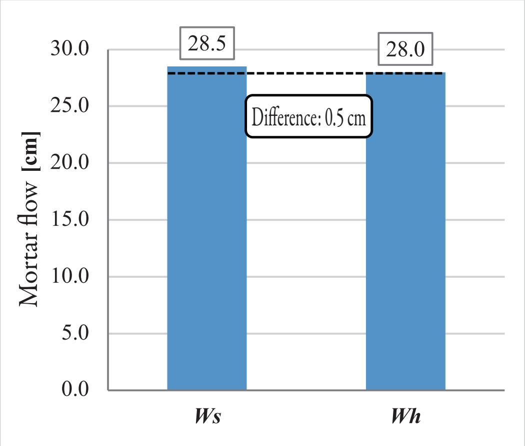


Figure 2: Difference in mortar flow values for the normal-strength concrete mix

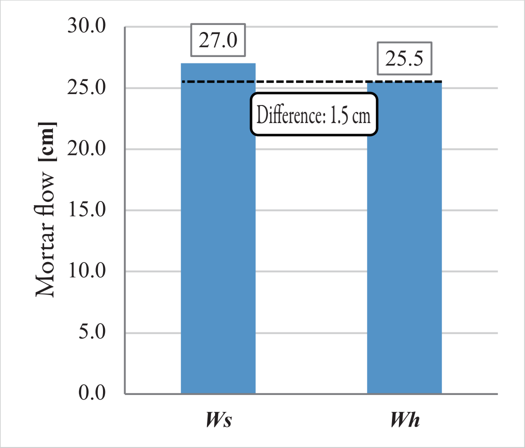


Figure 3: Difference in mortar flow values for the high-strength concrete mix

5. Effect of Twin-Shaft Forced Mixer on Concrete

The results in Section 4 show that the effects of mixing water could not be sufficiently identified through small-scale mixing using a Hobart mixer. In this section, a twin-shaft forced mixer, which more closely represents actual construction conditions, was employed to examine the effects of differences in the concentration of polyvalent cations in mixing water on the fluidity of concrete.

5.1 Experimental Overview

A twin-shaft forced mixer with a 60-L mixing capacity was used, and tests were conducted using two types of mixing water with various concrete mix designs. The quantities of each material were calculated for each mixture based on the specified mix proportions shown in **Tables 2** and **3**, and concrete was mixed accordingly. Due to the required mixer power, the mixing volume was set to 60 L, corresponding to the rated mixing capacity, for the normal-strength concrete mixtures, and to 36 L, which corresponds to 60% of the rated mixing capacity, for the high-strength concrete mixtures. The mixing procedures for the normal-strength and high-strength concrete mixtures are shown in **Figure 4**. Due to constraints in the mixing procedures, only slump was measured for the normal-strength concrete mixtures, whereas both mortar flow and slump flow were measured for the high-strength concrete mixtures.

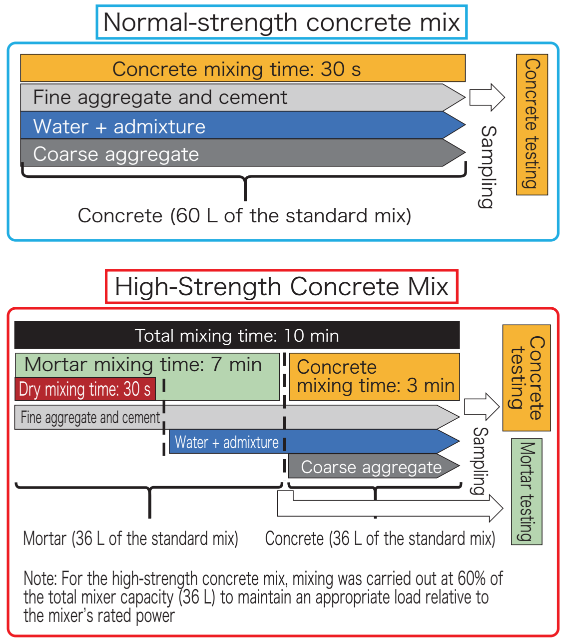
5.2 Slump of Normal-Strength Concrete Mixtures

The mixture used in this test was normal-strength concrete with a target slump of 18 cm, and the slump value was measured in accordance with the procedure specified in JIS A 1101.

Figure 5 shows the slump values obtained with each type of mixing water. The slump was 16.0 cm when *Ws* was used and 17.5 cm when *Wh* was used.

According to the quality control criteria specified in JIS A 5308, an allowable tolerance of ±2.5 cm is applied for target slump values in the range of 8–18 cm. The slump values obtained for both concrete mixtures in this study fall within the acceptable range and satisfy the specified control criteria.

Therefore, for the normal-strength concrete mixtures used in this study, the effect of changing the mixing water on the slump was not prominent, and polyvalent cations are considered to have little influence on concrete fluidity.



Note: For the high-strength concrete mix, mixing was carried out at 60% of the total mixer capacity (36 L) to maintain an appropriate load relative to the mixer's rated power

Figure 4: Mixing procedure using a twin-shaft forced mixer

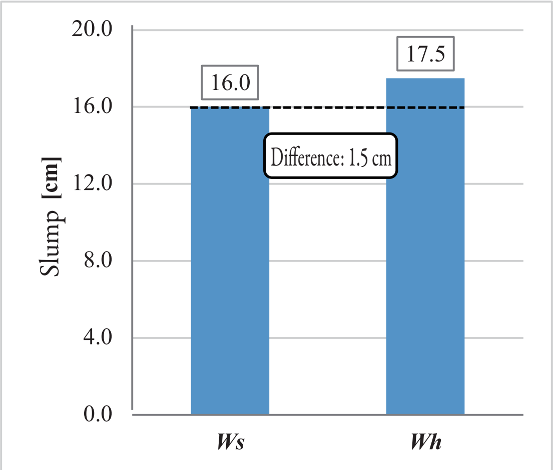


Figure 5: Difference in slump values for the normal-strength concrete mix

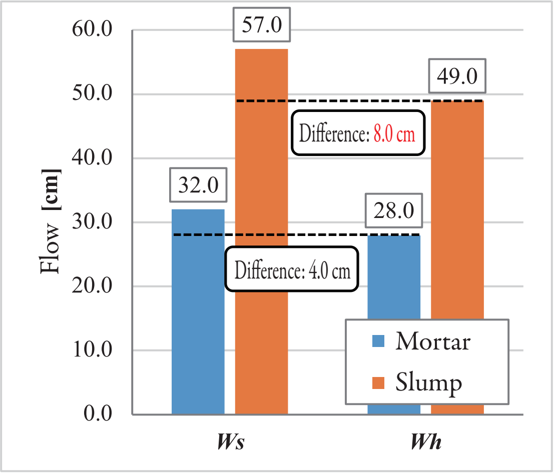


Figure 6: Differences in mortar flow and slump flow values for the high-strength concrete mix

5.3 Slump Flow of High-Strength Concrete Mixtures

The mixture used in this test was high-strength concrete with a target slump flow of 60 cm. Mortar flow was measured in the same manner as described in Section 4, while slump flow was measured in accordance with the procedure specified in JIS A 1150.

Figure 6 shows the mortar flow and slump flow values obtained with each type of mixing water. The slump flow was 57.0 cm when *Ws* was used and 49.0 cm when *Wh* was used. The difference in mortar flow values was smaller than that observed for slump flow; however, the trends for *Ws* and *Wh* were consistent with those of the slump flow results. According to the quality control criteria specified in JIS A 5308, an allowable tolerance of ±10 cm is applied for a target slump flow of 60 cm. Under this criterion, the concrete prepared with Ws falls within the acceptable range, whereas the concrete prepared with Wh falls below the allowable range. Therefore, for the high-strength concrete mixtures, changes in the mixing water had a clear effect on slump flow characteristics, suggesting that the concentration of polyvalent cations in the mixing water plays an important role in governing the fluidity of concrete.

6. Evaluation of Residual Admixture Ratio

The results presented in Sections 4 and 5 confirmed that polyvalent cations in the mixing water tend to cause a reduction in fluidity in high-strength concrete mixtures. In this section, focusing on the adsorption behavior of polycarboxylate-based admixtures as one of the contributing factors, the effects of polyvalent cations on the fluidity were investigated by measuring the residual ratio of admixtures in the liquid phase.

Our previous study7) has reported a correlation between the residual ratio of admixtures in the liquid phase and concrete fluidity. Accordingly, conducting a similar evaluation for the present phenomenon may be useful to discuss the influence of polyvalent cations on the fluidity.

6.1 Experimental Overview

For the high-strength concrete mixtures, mortar samples mixed using a twin-shaft forced mixer were collected and subjected to measurement. Sample collection was carried out during the mixing process for the high-strength concrete mixtures shown in **Figure 4**. As part of the measurement procedure, the samples were separated into liquid and solid phases using a centrifuge, and the extracted liquid phase was subjected to thermal analysis to determine the residual ratio of admixtures in the liquid phase.

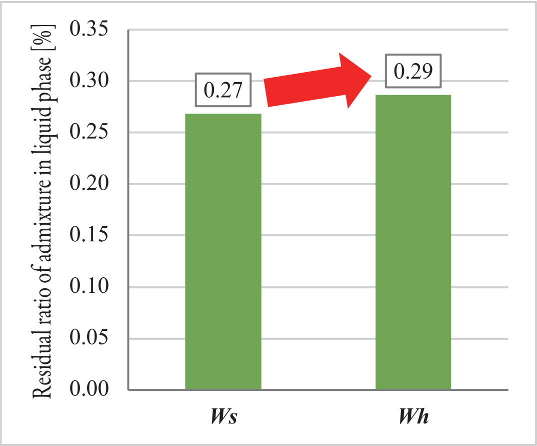


Figure 7: Residual ratio of admixture in liquid phase using twin-shaft forced mixer

6.2 Results and Discussion

Figure 7 shows the residual ratio of the admixture in mortar mixed using a twin-shaft forced mixer. The residual ratio of the admixture in the liquid phase of the mortar prepared with the mixing water *Wh* was higher than that of the mortar prepared with the mixing water *Ws*. This result exhibits an inverse correlation with the mortar flow presented in Section 5. The difference in the residual ratio of the admixture is comparable to that reported in a previous study7). The difference in the absolute values of the residual ratio from those reported in the previous study is considered to be attributable to differences in the mixing conditions.

From these results, it is inferred that the concentrations of Ca^{2+} and Mg^{2+} in the mixing water *Wh* were higher than those in the mixing water *Ws*, and that these polyvalent cations affected the dispersibility of the admixture. In contrast, as shown in Section 3 and based on comparison with previous studies, the influence of Na^{+} is considered to be small. Furthermore, as for other ions such as K^{+} and Fe^{2+}, it is presumed that the concentration differences between the two mixing waters are small, and that their effects on the fluidity are limited. Therefore, it is highly likely that polyvalent cations, mainly Ca^{2+} and Mg^{2+}, altered the adsorption behavior of the polycarboxylate-based admixture.

In the next section, the mechanism by which polyvalent cations influence fluidity is discussed from a chemical perspective.

7. Discussion on the Mechanism of Fluidity Reduction Caused by Polyvalent Cations

Figure 8 shows a schematic overview of the fluidity mechanism when mixing water containing a relatively low concentration of polyvalent cations is used. Based on this, **Figure 9** illustrates the effects of polyvalent cations in the mixing water as inferred from the results of the present study.

Polyvalent cations such as Ca^{2+} and Mg^{2+}, which are abundantly present in the mixing water, form complexes with the carboxyl groups of polycarboxylate-based admixtures and adsorb onto the surfaces of cement particles, which carry negative charges. After adsorption, the dispersibility of the cement particles is enhanced through steric hindrance.

However, when the concentration of polyvalent cations becomes excessive, these cations adsorb onto both the cement surface and the admixture molecules, resulting in both the cement surface and the carboxyl groups acquiring positive charges. Consequently, electrostatic repulsion occurs between the cement particles and the admixture, leading to reduced dispersibility and, in turn, decreased fluidity. Under such conditions, the admixture complexed with polyvalent cations does not adsorb onto the cement particle surfaces and instead remains in the liquid phase. This explains the increase in the residual ratio of the admixture in the liquid phase.

In contrast, for the normal-strength concrete mixture, an air-entraining (AE) water-reducing admixture was used. Its water-reducing performance is derived from a polycarboxylate ether; however, the admixture is designed to enhance fluidity retention rather than rapid fluidity development. Therefore, it is considered that the admixture does not immediately interact with the polyvalent cations in the mixing water, and the change in fluidity remained within a controllable range.

The results indicated that, beyond the range in which improved fluidity was confirmed in the previous study[3], changes in the adsorption behavior of the polycarboxylate-based admixture lead to a reversal of its effect on the fluidity.

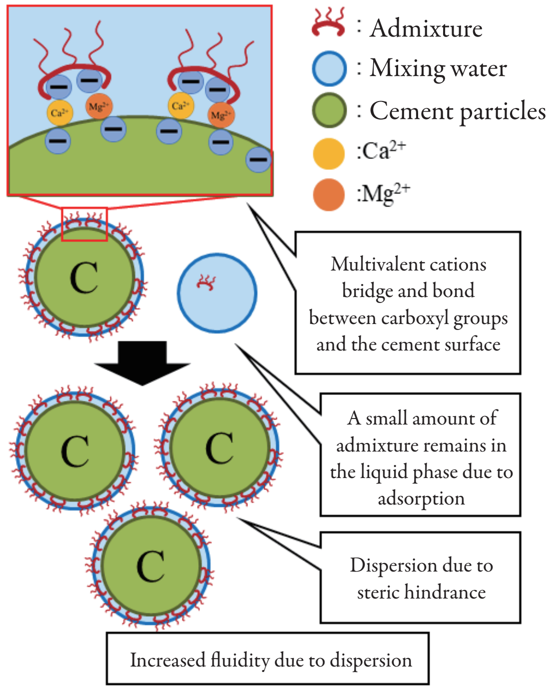


Figure 8: Mechanism of fluidity development

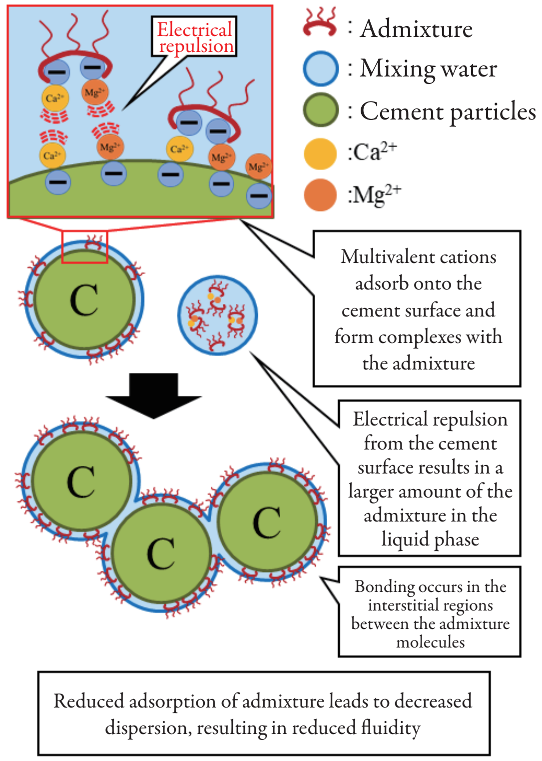


Figure 9: Mechanism of fluidity inhibition by multivalent cations

8. Conclusions

The findings of this study are summarized as follows.

(1) When the concentration of polyvalent cations in the mixing water was high, a consistent tendency was observed whereby the fluidity of mortar and concrete in high-strength concrete mixtures decreased with both the Hobart mixer and the twin-shaft forced mixer.

(2) The influence of polyvalent cations varied depending on the type of admixture and the water–cement ratio. In high-strength concrete mixtures using a polycarboxylate-based high-range water-reducing admixture, a significant reduction in fluidity was observed, whereas the effect was small in normal-strength concrete mixtures using an air-entraining (AE) water-reducing admixture.

(3) It is inferred that polyvalent cations adsorb onto both the carboxyl groups of the admixture molecules and the cement surface, thereby inhibiting the adsorption of the admixture and reducing fluidity.

From these results, it was clarified that mixing water having a concentration of polyvalent cations (Ca^{2+} and Mg^{2+}) comparable to that of the mixing water Wh used in this study affects the fluidity of fresh concrete in high-strength concrete mixtures.

However, previous studies have reported that an appropriate concentration of polyvalent cations can promote admixture adsorption and improve fluidity. Therefore, when the concentration of polyvalent cations is excessively high, reducing the polyvalent cation concentration may restore the fluidity of the concrete.

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