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EFFECTS OF MIXING AND TRANSPORTATION ON CHARACTERISTICS OF CEMENTITIOUS SYSTEMS CONTAINING FLY ASH

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ABSTRACT

According to the Portland Cement Association (PCA) (2000) over 50% of ready-mixed concrete currently contains fly ash. The use of fly ash is likely to increase because (1) the construction industry is attempting to become more sustainable; (2) fly ash can improve concrete performance; and (3) replacing cement with fly ash can reduce material costs. Fly ash-concrete systems are now becoming very common in our infrastructure systems.

Many concrete specifications place limits on the mixing and transportation of concrete systems. In fact, 48 of 50 State Highway Agencies (SHAs) place time limits on concrete placements and 30 of 50 SHAs place limits on the number of truck mixer drum revolutions. Few studies have been performed to assess whether these limits are applicable to concrete systems containing fly ash.

This paper presents the assessment of the influence of mixing time and number of revolutions on the characteristics of cementitious systems containing fly ash. The characterization methods evaluated in this study include the dissolution rate of hydroxyl ion, setting time, flowability, and compressive strength Results indicate that replacing cement with fly ash can reduce the negative effects on flowability and compressive strength resulting from increased mixing times and number of mixer revolutions. The limits of mixing time and number of revolutions of ready-mixed concrete from most SHAs are likely not applicable for cementitious systems containing fly ash and consideration should be given to modify these specifications.

INTRODUCTION

As sustainability becomes increasingly important to our society, more industries are focusing on developing or improving existing systems to make these systems more sustainable. The needs to preserve natural resources and to reduce energy consumption and CO_2 emissions have stimulated the development of using alternative resources [1, 2]. The construction industry is assessing a wide range of sustainability practices and products, with emphasis on using alternative resources and technologies, including the use of industrial by-products and agricultural wastes.

Fly ash is an industrial by-product from the coal combustion process for electricity generation. Currently, the coal combustion process accounts for 50% of the overall electricity generation in the U.S. [3]. Approximately 75% of the residues from the process are fly ash [4-6]. Hence, approximately 500 megatons of fly ash are generated at the power plants each year [7]. Fly ash is used in many applications including as a supplementary cementing material (SCM) in concrete, for agricultural and waste treatment, and for soil stabilization. However, at least 70% of the fly ash generated is not utilized and this becomes a serious problem for proper disposal [5, 8, 9]. Proper disposal of fly ash can be costly and is estimated to be approximately US$1.2 billion per year [10]. As the result, many industries and research are directed towards finding alternative methods of utilizing fly ash.

Besides water, concrete is the most widely used materials in the world [11]. Its production attributes 5 to 7% of the total man-made CO_2 emissions on earth [12]. Although efforts are beginning to reduce the CO_2 emissions from cement and concrete production, the CO_2 emissions from these industries are significantly high and more efforts are required. Fly ash is commonly used as a partial substitute for 15 to 25% of portland cement in concrete [13]. The American Coal Ash Association (ACAA) estimated that the use of fly ash as a cement substitute in concrete has the potential to eliminate 10 to 14 megatons of CO_2 emissions [14]. The partial replacement of fly ash as a source of SCM can significantly reduce not only the costs of producing concrete and disposing fly ash but also increase the sustainability by reducing CO_2 emissions. Dodson [15] reported that replacing cement with fly ash is expected to reduce materials cost approximately \$3.25 per m^3 of concrete. In addition to the reduction of costs, it is known that replacing cement with fly ash results in enhanced fresh characteristics, hardened performance, and durability of the end product. As a pozzolanic material, calcium hydroxide can be reacted to generate strength-enhancing calcium silicate hydrates, densifying the interfacial transition zone (ITZ) at the interface of cement and aggregate, and refining the concrete microstructure [11, 16, 17].

Ready-mixed concrete is widely used for many infrastructure systems. Specifications for ready-mixed concrete from the State Highway Agencies (SHAs), the American Society for Testing and Materials (ASTM), and the American Association of State Highway and Transportation Officials (AASHTO) provide similar requirement for mixing and agitating truck mixed concrete; specifically mixing time, number of revolutions, and temperature. In fact, 48 of 50 SHAs place time limits on a concrete placement, 30 of 50 SHAs place limits on number of truck mixer drum revolutions, and 45 of 50 SHAs place limits on temperature. Figure 1 shows placement limits as a function of mixing time and temperature from most SHAs. The limits of mixing time and number of revolutions of concrete systems are addressed by most SHAs because increased mixing time and number of revolutions of concrete systems result in the loss of the workability of fresh concrete mixtures. Loss of the workability makes concrete not castable or difficult to consolidate properly. Improper placement and consolidation can result in large voids in hardened concrete and can lead to significant reduction of compressive strength [18]. It is reported that the cost of finishing concrete is approximately 2 to 5 times higher than the material cost of making concrete [19]. Improved workability of fresh concrete likely leads to reduced finishing efforts, resulting in reduced construction costs.

Recent chemical technology proposed a set-retarding admixture to slow the hydration reactions of cement systems [20, 21]. Adding a set-retarding admixture into fresh ready-mixed concrete mixtures can stabilize the plasticity of fresh concrete for several hours. It is reported that the dosages of water-reducing admixtures are approximately 0.35 to 2.0% by weight of cement [22]. However, adding this admixture to suspend the set increases material costs [19]. An alternative approach that not only reduces the material cost but also improves workability of fresh concrete mixtures can significantly benefit the ready-mixed concrete industry.

The Portland Cement Association (PCA) [23] reported that more than 50% of ready-mixed concrete contains fly ash. Fly ash/concrete systems are now becoming very common in our infrastructure systems. The utilization of these systems tends to increase due to increasing in sustainability. However, limited studies have been investigated to evaluate whether these limits required by most SHAs are applicable to concrete systems containing fly ash. Therefore, this research presents the assessment of the effects of mixing time and number of revolutions on the performance characteristics of cementitious material systems containing 20 and 50% replacement of fly ash. The performance characteristics investigated in this research include the dissolution kinetics of hydroxyl ion, setting time, flowability, and compressive strength.

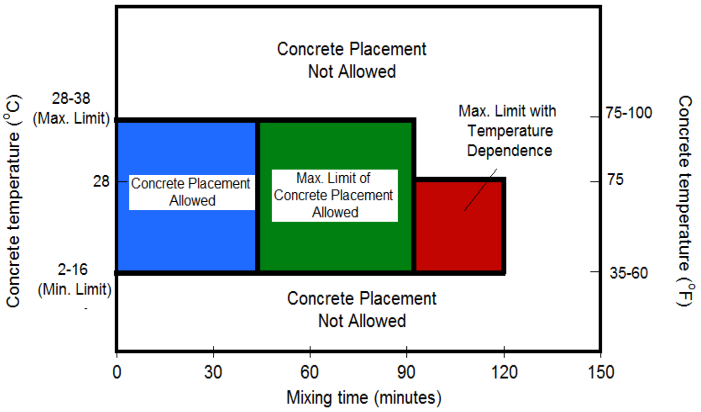

Figure. 1 Limits for placement of concrete as specified in most SHAs.

MATERIALS AND METHODS

Materials

Type I/II portland cement was used for all mixtures in this research. Class-F fly ash was procured from Centralia, WA. The chemical composition of portland cement and fly ash are shown in Table. 1. A Scanning Electron Microscopy (SEM) image of fly ash particles is shown in Figure 2. The observed particles of fly ash have spherical shape and smooth surface and contain wide range of particle size distribution. Ottawa graded sand meeting ASTM C778, *Standard Specification for Standard Sand*, was used for the flowability study. Fine aggregate, used for the compressive strength study, was obtained from a local source in Corvallis, OR and met ASTM requirement C33, *Standard Specification for Concrete Aggregates*. The fineness modulus of the fine aggregate was 2.5 determined following ASTM C136, *Standard Test Method for Sieve Analysis of Fine and Coarse Aggregates procedures.* The specific gravity of the fine aggregate was 2.47 and the absorption was 3.08%. The specific gravity and absorption were determined following ASTM C128, *Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate*. ASTM Type II de-ionized water (1 MΩ·cm at 25°C) was used for all mixtures and experiments.

Table. 1 Chemical composition of portland cement and class-F fly ash

Composition	Cement (%)	Fly ash (%)
SiO_2	20.3	51.5
Al_2O_3	4.80	16.9
Fe_2O_3	3.50	6.20
MgO	0.70	4.10
SO_3	2.80	0.70
CaO	63.9	11.7
Loss on Ignition	2.60	0.25
Insoluble Residue	0.11	-
Limestone	3.20	-
$CaCO_3$ in limestone	97.8	-
Na_{eq}	0.54	1.10

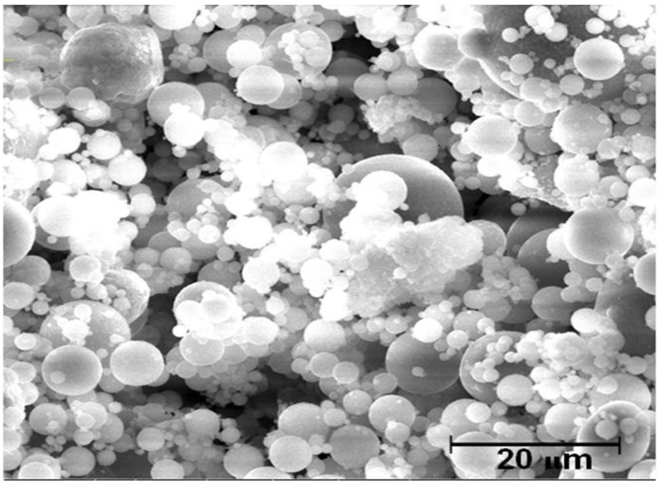

Figure. 2 SEM micrograph of fly ash particles.

Methods

This section consists of the preparation and characterization methods of fly ash/cement systems.

Preparation methods

The mixing procedure of the cement pastes and mortars followed ASTM C305, *Standard Practice for Mechanical Mixing of Hydraulic Cement Pastes and Mortars of Plastic Consistency*. The mixtures were prepared with 20 and 50% replacement levels of the fly ash. The authors proposed the evaluation of mixing with 50% fly ash because this % replacement level exceeds the normal range that fly ash is used. A control mixture (100% portland cement) was mixed and tested for comparison. ASTM C305 provides a mixing guideline for cement paste and mortar consisting of two stages: low speed (140 rpm) at the first stage and intermediate speed (285 rpm) at the second stage. The assessment of mixing processes was performed by adjusting the mixing time and mixing speed of the second stage. Table 2 shows the mixing conditions evaluated in this study. Three mixing times (2, 15, and 60 minutes) and two mixing speeds were evaluated. All test results are based on triplicate tests.

Table. 2 Mixing test parameters

Mixture No.	First stage		Second Stage	
	Mixing time (minutes)	Mixing speed (rpm)	Mixing time (minutes)	Mixing speed (rpm)
1	0.5	140	1.5	140
2	0.5	140	1.5	285
3	0.5	140	14.5	140
4	0.5	140	14.5	285
5	0.5	140	59.5	140
6	0.5	140	59.5	285

Characterization methods

Once the hydration process of cementitious systems begins, the concentrations of ions in solution change [24]. The hydroxyl ion concentration and related pH are important parameters that determine the reactivity of cement system. It is believed that fresh characteristics of cement such as setting time and flowability can be influenced by the concentrations of ions in solution. Many researchers [25-31] studied the effects of the concentrations of hydroxyl ions on the reactivity of SCM-based materials at early ages. The researchers reported that replacing cement with SCMs resulted in reduced concentration of hydroxyl ions in solutions. The replacement of cement with SCMs likely reduces the reactivity of hydration reactions. Shehata *et al.* [26] studied the relationship between the hydroxyl ion concentration of the pore solution and the level of replacement of three different fly ashes. The authors reported that fly ashes seemly acted as inert diluents. The concentrations of hydroxyl ion were evaluated in the study by measuring the pH level using a pH electrode and then determined as followed:

$$\text{Concentration of hydroxyl ion (mol/L)} = 10^{-(14-\text{pH})} \qquad (1)$$

The weight ratio of water-binder (w/b) of the solutions assessed was 4.0. Mixing for all systems was performed using a magnetic stirrer rotating at 0 and 400 rpm throughout the test. It is noted that for the mixtures mixed at 0 rpm, the solutions were first mixed at 400 rpm for 3 minutes and then mixing was stopped. The mixing of the first step allows cement particles to be mixed with water before assessing the different of mixing process. The time elapsed after introducing the cementitious materials to the solution is referred to here as the “hydration time.” Solutions for hydroxyl ions evaluated in this study were analyzed at 5, 10, 15, 30, 45, 60, 90, 120, 150, 180, 210, and 240 minutes.

The initial and final setting times of all systems were determined following ASTM C191, *Standard Test Methods for Time of Setting of Hydraulic Cement by Vicat Needle*. The w/b was 0.4 for all mixtures. The initial setting time refers to the time when the paste begins to stiffening and the final setting time refers to the time when the paste can support an external force without significant deformation [32].

The flowability of the cement mortars containing fly ash was determined following ASTM C1437, *Standard Test Method for Flow of Hydraulic Cement Mortar*. The w/b was 0.485 and the binder-fine aggregate ratio was 1:2.75, as recommended in the standard. In addition to the test program shown in Table 2, the 20 and 50% fly ash systems mixed for 90 minutes at the mixing speeds of 140 and 285 rpm were investigated in this test.

The 1-, 7-, and 28-day compressive strength of the mortars was evaluated following ASTM C109/C109M, *Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or [50-mm] Cube Specimens)*. The w/b of the mortars was 0.485. The binder-fine aggregate ratio was 1:2.75. After casting, test specimens were kept in plastic molds for 24 hours and then demolded. Demolded specimens were then cured in saturated-lime water until testing.

Two sample t-test and analysis of variances (ANOVA) analyses were performed to evaluate the samples with two groups and more than two groups, respectively. Prior to these analyses, the Shapiro-Wilk test was first used to analyze the normality of the data and the Levene's test was used to analyze the equal-variances of the data. The statistical hypotheses were defined as:

$$\text{Null hypothesis } (H_0) : \mu_1 = \mu_2 = ... = \mu_a \tag{2}$$

$$\text{Alternative hypothesis } (H_a) : \mu_1 \neq \mu_j \text{ for some } i \neq j \tag{3}$$

The 95% confidence interval was used for all analyses. If the H_0 is rejected (p-value ≤ 0.05), it is concluded that there is statistically significantly difference at the 5% level between the means of group populations. On the other hand, if the H_0 is not rejected (p-value > 0.05), it is concluded that there is no statistically significantly difference at the 5% level between the means of group populations.

RESULTS AND DISCUSSION

Concentration of hydroxyl ion

Unhydrated portland cement normally consists of large amounts of soluble alkali compounds. When introduced with water, the pH level of solution gradually rises and remains high [33]. This pH or the composition of solution affects the solubility of alkali compounds in the systems [34]. Figures 3*a)* and 3*b)* exhibit the influence of hydration time on the concentrations of hydroxyl ions in solutions mixed at 0 and 400 rpm, respectively. Results indicate that the concentrations of hydroxyl ions of all systems increase with increasing the hydration time. The slope of the fitted curve is referred to as the dissolution rate of the hydroxyl ions.

Figure 3*a)* indicates the slopes of the control, 20%, 50% fly ash systems are 9, 7.7, and 5.2 mmol/l/min, respectively. The larger slope of the control corresponds with that higher rate of dissolution of hydroxyl ions than the 20% and 50% fly ash, respectively. Results show that the dissolution rate of hydroxyl ion of the control mixed at 0 rpm is 14% and 42% higher than the 20% and 50% fly ash mixed at 0 rpm. Increased replacements level of fly ash of the systems lead to decreased dissolution rate of hydroxyl ions and this results in slower hydration reactions. The results in Figure 3*b)* were similar to the results in Figure 3*a)*, of which the slope of the control mixed at 400 rpm (17 mmol/l/min) is larger than the slopes of 20% (15 mmol/l/min), 50% fly ash (13 mmol/l/min) mixed at 400 rpm, respectively. For the systems mixed at 400 rpm the dissolution rate of hydroxyl ions of the control is 12% and 24% higher than the 20% and 50% fly ash. Increased replacement levels of fly ash result in slower rates of hydroxyl ions dissolution irrespective of mixing speed.

Comparing the slopes of the mixtures in Figure 3*b*) with the slopes in Figure 3*a*) indicates that the slopes of the control, 20%, and 50% fly ash mixed at 400 rpm were 89%, 95%, and 150% higher than the slopes of the control, 20%, and 50% fly ash mixed at 0 rpm, respectively. This indicates that mixing speed strongly affects the dissolution rate of hydroxyl ion of all systems and could affect early-aged characteristics of mixtures. Mixing speed increasingly affects the dissolution rate of hydroxyl ion when the systems contain higher replacement levels of fly ash.

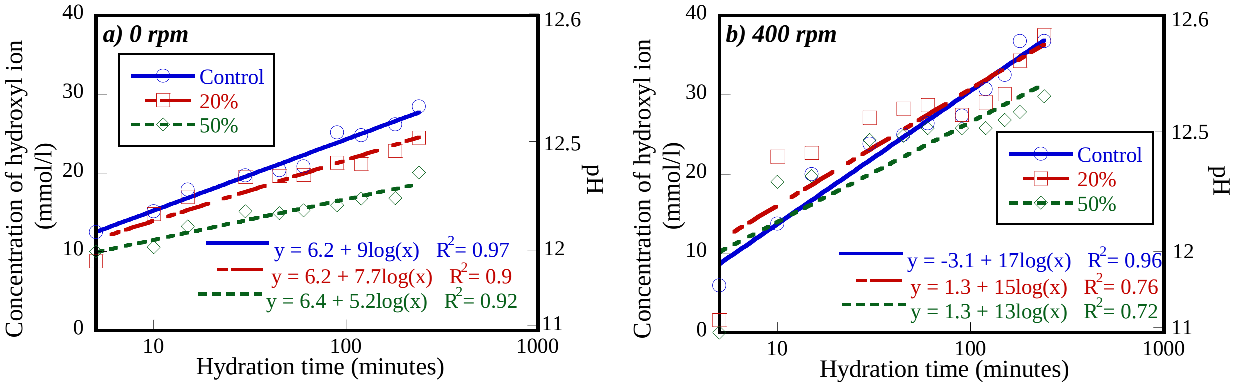

Figure. 3 Effect of hydration time on concentration of hydroxyl ion mixed at *a)* 0 rpm and *b)* 400 rpm.

Setting time

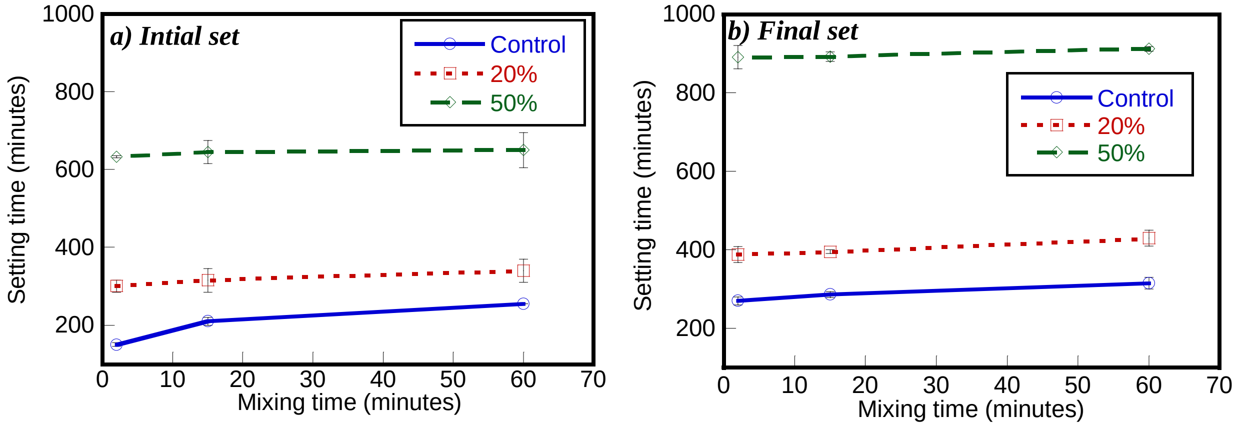

Figure. 4 Effect of mixing time on *a)* initial and *b)* final setting time mixed at 285 rpm.

The influence of mixing time on the initial and final setting times of the control, 20%, and 50% fly ash systems is shown in Figures 4*a)* and 4*b*). Results indicate that increased levels of fly ash replacement result in delayed setting times. The delaying effect is likely due to the adsorption of calcium ions on the surface of fly ash [35] and lowered hydroxyl ion concentration. It is believed that a reduction of calcium ion concentrations in solution is a result of the absorption of calcium ions and this leads to delayed nucleation and precipitation process of the calcium hydroxide, calcium silicate hydrates, and ettringite. Results also show that increased mixing time leads to increased initial and final setting times of the paste. This is likely because the constituent's particles are still deformed by a movement of mixing tools during continued mixing. This deformation of the particles likely interrupts the adhesion bonding of small particles to form a larger structure. Therefore, during this period, the hydrating particles lose their ability to support a load leading to delayed setting. After the mixing process discontinues, the adhesion bonding can begin to form as a larger structure and this structure, with time, can support loads. However, it is believed that part of water is reacted during mixing and this leads to less amounts of water available for flow before casting and consolidating the material.

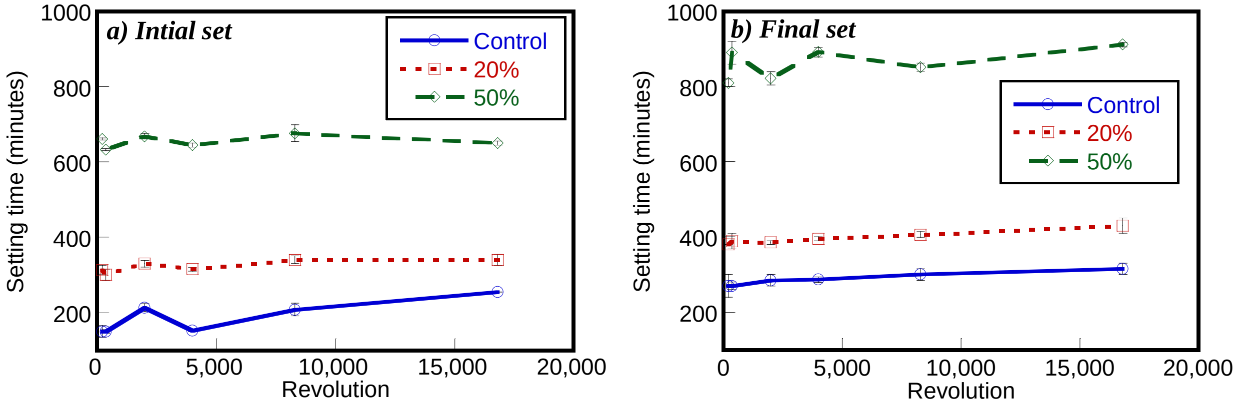

Figure. 5 Effect of number of revolutions on *a)* initial and *b)* final setting time.

Figures 5*a)* and 5*b*) show the effects of initial and final setting time versus number of revolutions, respectively. Results indicate that the initial and final setting times of the control, 20%, and 50% fly ash systems tend to increase as a function of number of revolutions. Increased mixing time and number of revolutions leads to delayed setting times of cement systems containing fly ash.

Flowability

Effects of mixing time on flow of the control, 20%, and 50% fly ash are shown in Figure 6. Results indicate that the flow of all systems is reduced as a function of mixing time. An increase in replacement level of fly ash results in increased flow. The flow of the fresh mortars of the 20% and 50% fly ash mixed for 2 minutes exhibited 12% and 31% larger flow than the control, respectively. The flow of the fresh mortars of the 20% and 50% fly ash mixed for 15 minutes exhibited 30% and 48% larger flow than the control, respectively. The flow of the fresh mortars of the 20% and 50% fly ash mixed for 60 minutes exhibited 50% and 43% larger flow than the control, respectively. In addition, results show that the percent replacement of fly ash allows mixing time to have less effect on flow. The flow of the 50% fly ash mixed for 2 and 15 minutes was 16% and 14% higher than flow of the 20% fly ash. The flow of the 50% fly ash mixed for 60 minutes was 5% less than flow of the 20% fly ash. There is no significant difference in flow between the 20 and 50% fly ash when mixed the mortars for 90 minutes (two-sample t-test = 0.209).

It should be noted that control mixtures were discontinued when mixed for 60 minutes but the 20% and 50% fly ash mixtures could be mixed longer periods, up to 90 minutes. The control began to stiffen and was unable to be casted after mixing for 60 minutes due to the reduction in flow and the progress of hydration reactions. In this study, replacing cement with fly ash can extend the mixing time. As hydrating products form, the early stiffening behavior is controlled by the gradual loss of free water from hydration reactions [36].

It is reported that flowability of fly ash/cement systems is influenced by size distribution, morphology, surface condition, fineness, and loss on ignition of the fly ash particles [37]. Replacing cement with fly ash is believed to make more water available for flow. Gopalan [38] reported the water absorption characteristics of the cementitious systems are reduced when fly ash is present. In addition, the spherical particles and better particle size distribution of fly ash (which is shown in Figure 2) lead to the reduction in friction between constituent particles in the systems (this commonly known as the “ball-bearing effect”) [31, 39-41]. Thus, although increased mixing time reduces the flow of the fly ash/cement systems, the materials can be mixed longer and still be castable due to improved flow. Based on test data, specification’s limits on mixing time may not be appropriated when fly ash is present in the cementitious systems.

The plot of the flow of fresh mortars as a function of number of revolutions is shown in Figure 7. Results indicate the flow of the control, 20%, 50% fly ash systems is significantly reduced with increasing number of revolutions. The flow of the control is less than the flow of the 20 and 50% fly ash, respectively. Increased replacement levels of fly ash allow the systems to absorb less water leading to enhanced flow. Replacing cement with fly ash increases the flow with increasing number of mixer revolutions.

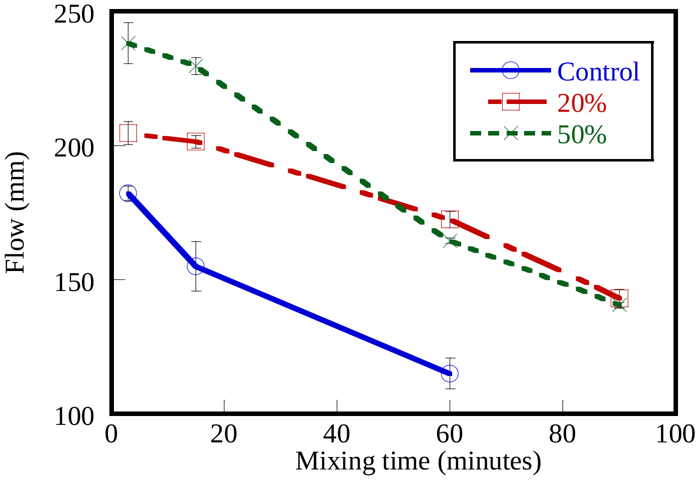

Figure. 6 Effect of mixing time on flow mixed at 285 rpm.

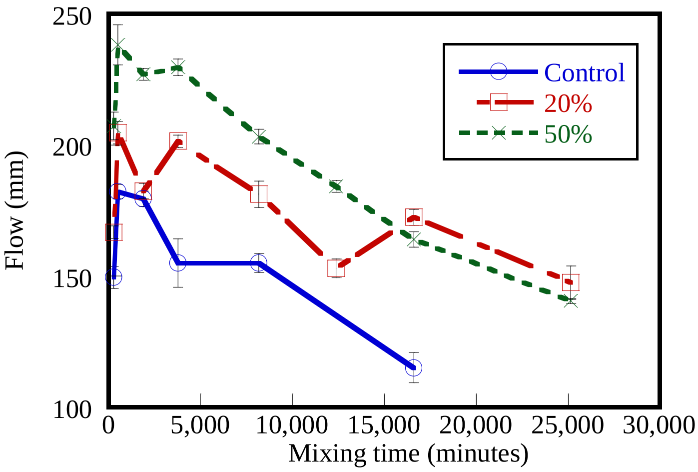

Figure. 7 Effect of number of revolutions on flow.

Compressive strength

There is no clear consensus in the literature regarding compressive strength of concrete systems with increasing mixing time [22, 42-45]. Some researchers reported significant reductions in compressive strength with increasing mixing times [22, 46]. These contradictory findings require clarification. Figures 8*a)* to 8*c)* show the influence of mixing time on the 1-, 7-, and 28-day compressive strength, respectively. Results show that the 1-, 7-, and 28-day compressive strength is significantly reduced with increasing percent replacement of fly ash. This is commonly caused by lowered cement contents in the fly ash systems. It is noted that the reduction of 28-day compressive strength with increasing mixing time of the control was observed, but statistically there is no significant effect (ANOVA test with p-value = 0.07). The control systems mixed for 2, 15, and 60 minutes exhibited no significant difference in the 1-, 7-, and 28-day compressive strength (ANOVA test with p-value = 0.99, 0.957, and 0.07, respectively). The 1-day compressive strength of the 20% fly ash mixed for 60 minutes was 49% and 52% higher than the 1-day compressive strength of the 20% fly ash mixed for 2 and 15 minutes, respectively (ANOVA test with p-value = 0.05). The 7- and 28-day compressive strength of the 20% fly ash exhibited no significant difference with increasing mixing time from 2 to 60 minutes (ANOVA test with p-value = 0.059 and 0.688, respectively). For the 50% fly ash, the results exhibited a significant increase on the 1-, 7-, and 28-day compressive strength (ANOVA test with p-value = 0.003, 0.049, and 0.007, respectively). The increase of compressive strength with increasing mixing time may be caused by the microstructure change [47], the decrease of air content [48], and/or the depletion of mixed water due to hydration reactions prior to casting the specimens [44, 45].

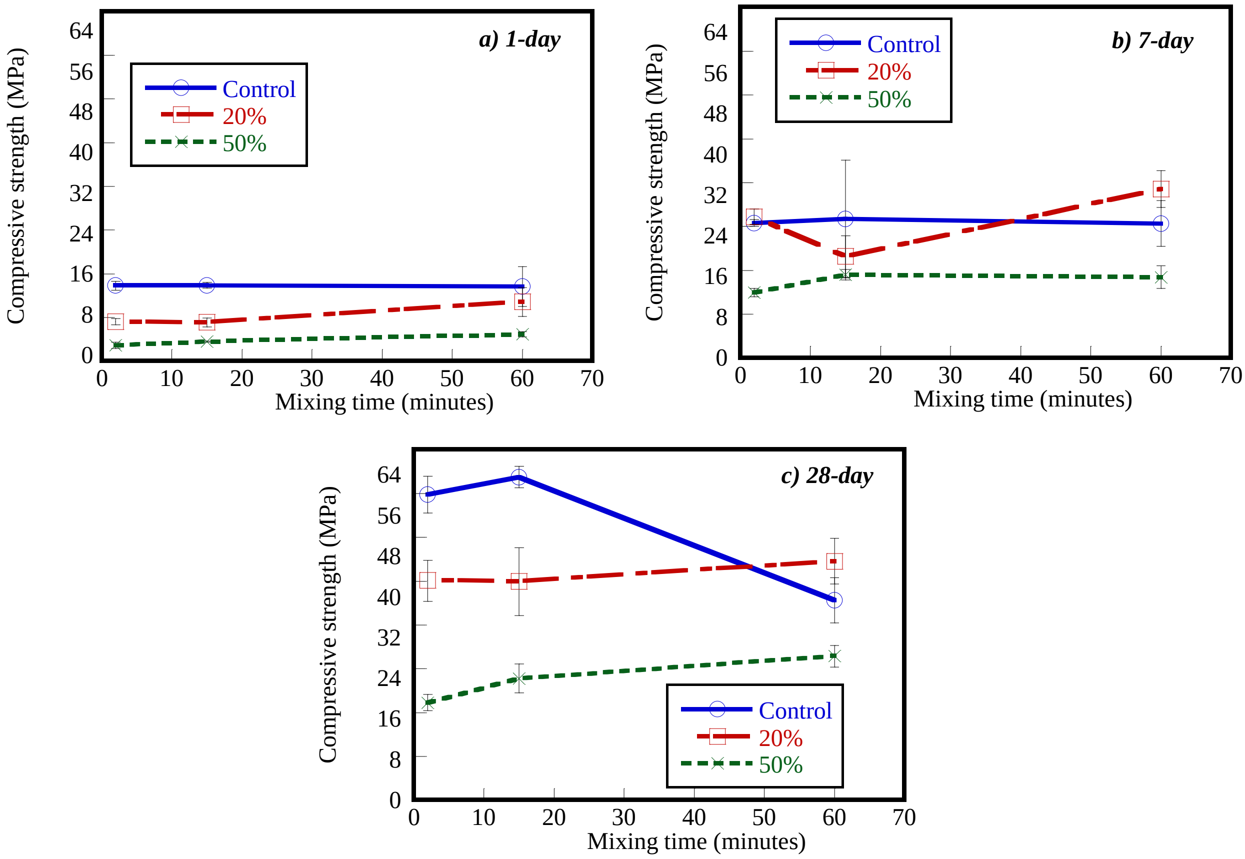

Figure. 8 Effect of mixing time mixed at 285 rpm on *a)* 1-, *b)* 7-, *c)* and 28-day compressive strength.

Based on test results, the mixing time of the 50% fly ash mixtures has greater influence on the 1-, 7-, and 28-day compressive strength than the 20% fly ash and the control. Increased mixing time of the cementitious systems containing fly ash seemingly improves the compressive strength.

The effects of the 28-day compressive strength of all systems as a function of number of revolutions are shown in Figure 9. Results indicate that the 28-day compressive strength of the control is reduced with increasing number of mixer revolutions (ANOVA test with p-value = 0.004). However, the 28-day compressive strength of the cementitious systems with 20% and 50% fly ash increases as the number of revolutions increase (ANOVA test with p-value = 0.001 and 0.05, respectively).

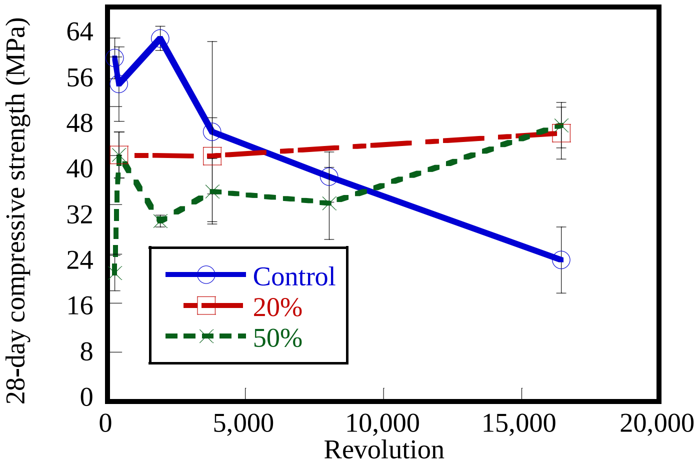

Figure. 9 Effect of number of revolutions on 28-day compressive strength.

CONCLUSIONS

The study assessed the influence of mixing time and number of mixer revolutions on the performance characteristics of cementitious systems containing fly ash. The dissolution rate of hydroxyl ion, setting, flowability, and compressive strength were assessed for different mixing times and number of mixer revolutions. Results indicate that increased mixing speed also leads to an accelerated dissolution reaction of hydroxyl ion in solutions. Increased replacement levels of fly ash lead to improved flowability and compressive strength, but delayed the set and hydration reactions. Increasing mixing time and number of mixer revolutions results in decreased flowability, increased setting time, and enhanced 28-day compressive strength when fly ash is present in the system. Based on test results, limits for mixing time and number of mixer revolutions of existing specifications from most SHAs may not be applicable to the cementitious systems containing fly ash. Research is on-going to further study of performance characteristics of fly ash/cement systems as a function of mixing time and number of revolutions and the effect of truck mixer revolutions of flow, set time, and compressive strength still needs to be assessed.

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