

Experimental and SEM Analyses of Ground Fly Ash in Concrete

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Abstract: Fly ash is used in concrete to improve the fresh and hardened properties of concrete, including workability, initial hydration temperature, ultimate strength and durability. A primary limitation on the use of large quantities of fly ash in blended cement concrete is its slow rate of strength gain. Prior studies investigated the effects of grinding fly ash and fly ash fineness on the performance of concrete containing fly ash. This study aims to discover the sources of those effects, to verify the compressive strength behavior of concrete made with raw and processed Class C fly ash, and to investigate the properties of fly ash particles at the microscopic level. Concrete cylinder test results indicate that grinding fly ash can significantly benefit the early age strength as well as the ultimate strength of concrete with ground fly ash. Therefore, it is demonstrated that grinding fly ash increases its reactivity. Scanning Electron Microscopy was then used to investigate the physical effects of the grinding process on the fly ash particles in order to identify the mechanism by which grinding leads to improved concrete properties.

Keywords: fly ash, scanning electron microscopy, blended cement concrete

1. Introduction

Fly ash is a glassy, spherical, and non-combustible portion of coal, generated in coal combustion power plants. It forms when melted glassy, spherical particles collide and form large, irregularly shaped particles as they cool and solidify in the boiler exhaust. The fly ash is collected from filtering systems that remove the solid particles from the exhaust of the power plants and either dispose of or incorporate it into other materials, such as blended cements. Because it is a waste product, the properties of fly ash are highly variable according to the type of coal, amount of oxygen, and burning methods in the combustion chamber at a particular facility.

In portland cement concrete, fly ash is often used to improve the fresh and hardened properties of concrete. The desirable properties obtained by using fly ash include improving the workability of fresh concrete, reducing the initial hydration temperature in mass-concrete applications, increasing the sulfate and chloride resistance of the resulting reinforced concrete, and improving the ultimate strength of the concrete.¹

Class C fly ash has both cementitious and pozzolanic properties, meaning that it can react with water as well as with calcium hydroxide in a portland cement concrete mixture to produce calcium silicate hydrates. This allows it to replace a portion of the portland cement in a blended cement without loss of long-term

strength. Because portland cement manufacturing releases large amounts of carbon dioxide, the use of fly ash to replace portland cement has environmental benefits beyond the reuse of a waste material. However, the hydration reaction of fly ash particles is generally slower than traditional portland cement. Because of this slower hydration reaction, concrete made with fly ash typically exhibits a lower compressive strength at early ages. As a result, replacing significant portions of the portland cement with fly ash may cause construction to be delayed in order for the concrete to reach the necessary strength prior to removal of shoring or proceeding with construction.

Several hypotheses have been proposed to describe the delayed strength gain commonly observed when significant quantities of fly ash are used in portland cement concrete. Most researchers suggest that the reactive portion of the fly ash is made unavailable either because there are very few reaction sites available on the smooth, spherical particles or that an insoluble barrier is present on the surface of the particles.

Several studies²⁻⁶ have been conducted in recent years to monitor the influence of fly ash and its size distribution on the compressive strength of the fly ash concrete. These studies have considered changes in the size distribution of the material by separating the relatively fine and coarse particles in a sample and by grinding the fly ash; however, many of these studies have considered only Class F fly ash produced outside North America.

According to Slanika,² the fineness of fly ash particles is a key element to long term compressive strength gain of concrete made with fly ash. Slanika² also pointed out that due to the low cementitious properties of coarse fly ash, this ash is generally used as a substitute for fine aggregate or to correct for the unsuitable shape or grading of fine aggregates. Use of fly ash in concrete is not generally economical unless fine fly ash can be substituted for fair portions of the portland cement.² Berry³ proposed that coarse fly

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ash exhibits low pozzolanic activity due to a high percentage of insoluble crystalline phases and concluded that due to these crystalline phases, coarse fly ash should not be used in concrete. Tan and Pu⁴ ground fly ash in a ball mill to a Blaine fineness of 6021 cm²/g. Their results showed small changes in concrete compressive strength at an early age of 72 hours; however, significant compression improvement appeared at 28 and 56 days.

Kiattikomol *et al.*⁵ determined the Blaine fineness of traditional portland cement, unprocessed fly ash, and coarse fly ash to be 3,230, 2,370, and 940 cm²/g, respectively. Kiattikomol *et al.*⁵ were able to grind fly ash to a fineness of 8800 cm²/g. This study concluded that the grinding converts spherical fly ash particles to irregular and crushed shaped particles, increasing their reactivity. Chindaprasirt *et al.*⁶ separated fly ash into various levels of fineness by using an air classifier machine. The results showed that the concrete pastes containing the finer fly ash have a higher compressive strength, lower total porosity and capillary porosity than those with the original fly ash.

Based on the results of dissolution experiments, Brouwers and Van Eijk⁷ presented a mathematical model describing fly ash as a two-component, perfectly spherical particle with material deposited in uniform layers. In this model, the outer layer consists of non-reactive glasses, including K₂O, Na₂O, CaO, MgO, and Fe₂O₃. The core of the fly ash particle is much more reactive, but cannot begin to hydrate until the outer shell has dissolved, and consists primarily of SiO₂ and Al₂O₃.

Fu *et al.*⁸ examined circulating fluidized bed combustion (CBFC) fly ash, which contains more angular and irregularly shaped particles than other fly ashes, using several methods to evaluate the effects of grinding on the particles. While mortar or concrete samples were evaluated to determine the effects on the strength of the resulting paste, changes in the properties of the material that are associated with an increased rate of strength gain were identified. It was found that most changes in the size distribution and reactivity occur during the first 30 minutes of grinding, with reduced benefits from longer grinding periods. Using pH analysis of thin pastes made with fly ash and water, the grinding process was found to increase the reactivity of the fly ash significantly. Two primary mechanisms were proposed for this increase. First, the grinding process crushes Calcium Sulfate layers, releasing the Calcium Oxide for more rapid dissolution and increased reactivity. Second, the grinding process converts small amounts of crystalline phase materials into more reactive amorphous phases.

2. Research significance

As reviewed in the introduction, many researchers³⁻⁷ have investigated the effects of grinding the fly ash and fly ash fineness on the performance of concrete using significant amounts of fly ash; however, the sources of those changes have not been well described. The objective of this research is to investigate the properties of fly ash particles at the microscopic level while verifying the compressive strength behavior of concrete made with the investigated fly ash.

3. Experimental study

An experimental study was conducted to investigate the

changes in the fly ash particle size distribution and the topography of the fine particles due to grinding along with the effect of these changes on the early and ultimate strength of concrete incorporating this processed fly ash.

3.1 Materials

Type-I portland cement from the Holcim, Inc. plant in Midlothian, Texas, Class C fly ash from Red Rock, Oklahoma, and tap water were used in this research. The coarse aggregate used in this research was 21 mm maximum size gravel, and the fineness modulus of fine aggregates was 2.5. A carboxylate superplasticizer was used to increase the workability of all mixtures.

Red Rock fly ash is widely used by the Oklahoma Department of Transportation (ODOT) in concrete pavements. The power plant that produces this fly ash uses a dry process and burns a blend of native (Oklahoma) coal and Wyoming sub-bituminous coal. The results of this study are specifically derived from the Red Rock power plant fly ash and may not be applicable to fly ash from other sources.

The fly ash used in this study was ground in a ball mill for 30 and 120 minutes and replaced 0% and 20% of the portland cement by weight. To determine the effectiveness of grinding the fly ash, the Blaine fineness of each sample was measured. The effect of grinding on the physical properties of fly ash particles is tabulated in Table 1. A chemical analysis of the fly ash particles showed no significant change to the chemistry of the material. The results of chemical analysis are tabulated in Table 2.

3.2 Mix proportions

All of the concrete samples were made using the same quantity of cementitious materials at 356 kg/m³, and a similar water to cementitious material ratio of 0.35. The amount of superplasticizer was kept constant in all mixes to allow monitoring of the effect of fly ash on the workability of the concrete.

Aggregates were collected and kept in a sealed container to prevent water content changes. The water content of aggregate was

Table 1 Physical properties of portland cement and fly ash.

Parameter	Cement	Fly ash grinding duration (min)		
		0	30	120
Blaine fineness (cm ² /g)	-	5,110	5,240	5,385
Mean particle size (μm)	18.75	20.87	15.91	16.67
Mode (μm)	21.69	23.81	19.76	21.69
STDV (μm)	14.37	25.42	19.95	19.95

Table 2 Chemical composition of portland cement and fly ash.

Parameter	Cement	Fly ash grinding duration (min)		
		0	30	120
Silicon dioxide, SiO ₂	19.90	37.34	37.23	36.81
Aluminum oxide, Al ₂ O ₃	4.70	17.72	17.74	17.31
Iron oxide, Fe ₂ O ₃	3.45	6.25	6.27	6.22
Calcium oxide, CaO	64.14	25.68	25.54	25.74
Magnesium oxide, MgO	0.77	5.44	5.40	5.40
Sodium oxide, Na ₂ O	0.16	1.90	1.90	1.90
Potassium oxide, K ₂ O	0.77	0.53	0.53	0.53
Sulfur trioxide, SO ₃	2.81	1.59	1.59	1.59
Loss on ignition, 750°C	-	0.30	0.33	0.33
Loss on ignition, 1,000°C	2.43	0.38	0.41	0.41

Table 3 Mix proportion of the concrete studied

Mix No.	Fly Ash Content (%)	Grinding Duration (min)	Portland Cement (kg/m ³)	Fly Ash (kg/m ³)	Sand (kg/m ³)	Course Aggregate (kg/m ³)
1	0	---	356	---	916	1051
2	20	0	285	71	904	1051
3	20	30	285	71	893	1051
4	20	120	285	71	882	1051

calculated daily and prior to batching. Concrete samples were cast in 102 × 203 mm cylinder molds, and kept in the controlled environmental chamber with constant humidity and temperature of 50% and 23.5°C (74.3 °F). Table 3 presents the mix proportions studied.

3.3 Grinding system

A concrete mixer and steel grinding media were used to grind the fly ash. The media had diameters ranging from 16 to 38 mm. The mixer drum was loaded with 14 kg of grinding media, 4.5 kg of fly ash and 50 ml of Propylene Glycol, a grinding agent used to reduce caking.

4. Test results and discussion

4.1 Effects of grinding on compressive strength

The results of the concrete compressive strength tests are presented in Fig. 1. As expected, the replacement of 20% of the portland cement with un-ground fly ash reduced the compressive strength of the specimens at all ages. The samples with un-ground fly ash exhibited 11.6 and 5.8 N/mm² lower compressive strength than 100% portland cement samples at 3 days and 28 days, respectively.

The samples replacing 20% of the portland cement with fly ash ground for 30 minutes had compressive strengths 7 and 8.3 N/mm² higher than the samples with un-ground fly ash at 3 days and 28 days, respectively. These samples had compressive strengths 4.7 N/mm² lower than the 100% portland cement concrete at 3 days, but they exhibited slightly higher strength (2.5 N/mm² higher) than 100% portland cement concrete at 28 days. These tests indicate that grinding the fly ash can significantly benefit the early age strength as well as the ultimate strength of the samples.

4.2 Effects of grinding on large particles

Figure 2 shows the size distribution of fly ash particles before and after grinding. The size of fly ash particles was measured from SEM images. There is a shift in the size distribution curve of fly ash after grinding due to crushing of the coarse particles. This indicates that grinding decreases the volume of particles greater than

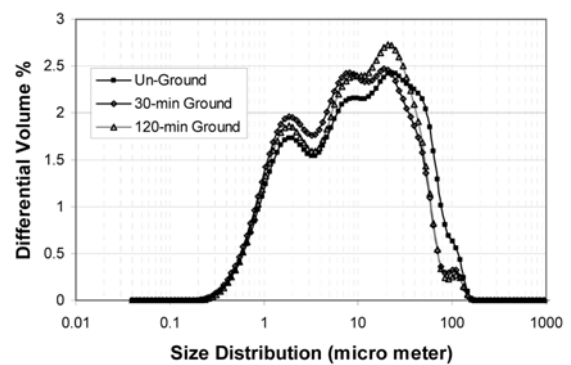
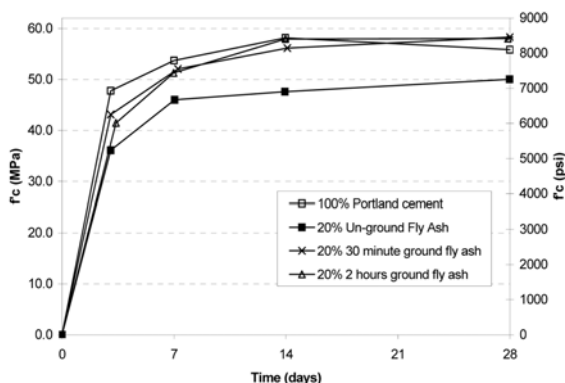
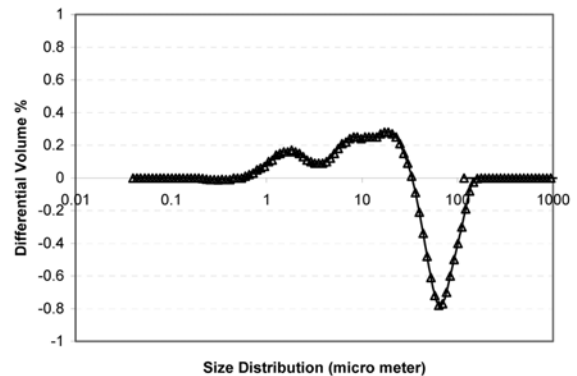
40 µm in the sample. These particles are only 16% of the volume of the un-ground sample and this volume declines to 9% after grinding. The volume shift at each particle size after 120 minutes of grinding is shown in Fig. 3.

4.3 Effects of grinding on small particles

Size distribution analysis showed that the grinding system used in this system did not significantly affect the size of particles smaller than 40 µm. Additionally, the Blaine fineness results summarized in Table 1 indicate no significant change in the fineness of the fly ash particles due to grinding. To better understand the mechanism involved, it was necessary to investigate the effect of grinding on individual particles. To achieve this goal, Scanning Electron Microscopy (SEM) analysis was performed on the fly ash samples.

The SEM results indicate that nearly all of the particles were spherical in shape, but none of the surfaces were perfectly smooth. In particular, no cleaved particles were found. Figure 4 shows typical groups of particles at low magnification.

The results of the compressive strength tests indicate that most of the benefits of grinding were achieved after grinding the fly ash for 30 minutes. Therefore, the un-ground sample and 30 minute ground fly ash samples were carefully compared under the microscope to search for indications of the physical effects of the grind-

**Fig. 2** Particle size distribution of fly ash.**Fig. 1** Effects of ground fly ash on compressive strength.**Fig. 3** Volume shift after 120 min grinding.

ing operation. The most obvious difference was that grinding appeared to remove the bumps from the surfaces of the particles. High magnification images of two particles are shown in Fig. 5.

To quantify this trend, a selection of individual particles in each sample with diameters between 5 and 6 μm were determined and photographed at a magnification of 14000x. Borrowing a technique used in microbiology, the percentage of a 1 μm square centered on the particle that was covered with these bumps was counted on each image. Particles of similar size were used to minimize differences in curvature within the area counted. A T-test was used to determine that the ground sample did have a significantly lower surface bump density with at confidence of 99.1%. The average bump density of the fly ash particles was reported as 48.46 and 32.82 for un-ground and 30 minute ground fly ash, respectively. Figure 5 shows typical particles from each sample.

5. Conclusions

In this study, an experimental program was carried out to verify the effect of grinding on the compressive strength of concrete made with fly ash and to investigate the properties of fly ash particles at the microscopic level. Both conventional concrete cylinder compression tests and novel Scanning Electron Microscopy analyses were used. Based on these tests and analyses, the following conclusions are made:

- 1) Grinding the fly ash can significantly benefit the early age strength as well as the long-term strength of concrete. This demonstrates that grinding fly ash increases its reactivity, allowing for increased substitution of fly ash for portland cement.
- 2) Grinding the fly ash decreases volume of particles greater than 40 μm , breaking them up into smaller particles.

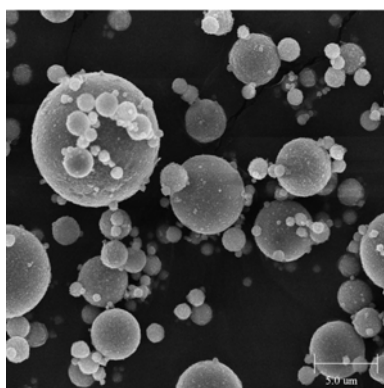
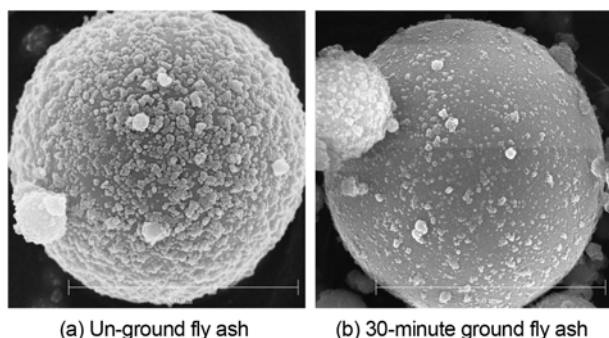


Fig. 4 Typical fly ash particles at low magnification.



(a) Un-ground fly ash

(b) 30-minute ground fly ash

Fig. 5 Typical fly ash particles.

3) Grinding the fly ash removes a surface layer from particles in the range of 5 to 6 μm .

4) The reactivity of fly ash may be increasing due to both 1) removal of a dissolution barrier on the small fly ash particles and 2) increased reaction sites on the larger particles.

5) The two-component, perfectly spherical particle mathematical model of fly ash with material deposited in uniform layers proposed by Brouwers and Van Eijk² is appropriate for small diameter fly ash particles, though the uniformity of the layers may be questionable.

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