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Permeability of Ultra-Fine Reactive Fly Ash applied to Cement-Based Composites

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Abstract. *This study explores the permeability of the partial replacement of cement using ultra-fine reactive fly ash (URFA) and silica fume. URFA is an industrial by-product from thermal power plants and it has a smaller spherical particle size (0.1 µm to 10 µm) than the general fly ash. The fixed water-to-binder ratio was 0.45 and the replacement of cement was used as 5% and 10%. The combinations of URFA and silica fume in composites were used as 5% URFA plus 5% silica fume and 8% URFA plus 2% silica fume. The results show that the inclusion of URFA was enhanced to increase the workability, and help to produce pozzolanic reaction and C-S-H colloids. The colloids were filling the pore structures to increase the compactness of specimen, which is consistency with the increased the compressive strength and reduction of the dry shrinkage. It also was reduced the chloride ion penetration and non-steady state migration coefficient, which is helpful for improving the mechanical properties and permeability. The composites with 10% URFA had a better performance. For blending specimen, it was also a tendency to improve mechanical properties and permeability; and the combination of 5% URFA and 5% silica fume in composites enhanced better performances.*

Keywords: *Ultra-Fine Reactive Fly Ash, Chloride Diffusion, Durability, Pore Structures.*

1 Introduction

Fly ash is a popular pozzolanic material with high SiO_2 and Al_2O_3 content. When cemented with water, the cementing performance is relatively low (Yang et al., 2018), but it will be activated by hydroxide ions (OH^-). Fly ash is usually added to cement as a pozzolana because it can be cured in wet conditions or underwater and further protect hardened materials from chemical attack. In most cases, fly ash is obtained from thermal power stations and is recycled as a pollution control measure, usually blended with ordinary cement to improve cement performance (Li *et al.*, 2014).

Fly ash is sufficiently reactive when it reacts with water and CaO in the cement (Telesca *et al.*, 2017). At room temperature, C–S–H gels are formed in the internal structure of the mixture, thereby forming hydraulic cementitious materials (Temuujin *et al.*, 2009; Duan *et al.*, 2017). Fly ash is also used to improve the performance of concrete in the fresh and hardened state, for improving workability, attaining high compressive strength at the early age, achieving long-term compressive strength, low drying-shrinkage and creep coupled with excellent durability properties (Zuquan *et al.*, 2007; Xu *et al.*, 2017; Ahmad *et al.*, 2019; Tan *et al.*, 2019).

Several prominent researchers have devoted time to exploring the characteristics and application of fly ash in cementitious materials over the years and the general categories in which fly ash can be grouped regarding its effect on concrete includes morphological, active and micro-aggregate effects (Aiqin *et al.*, 2003; Aiqin *et al.*, 2004; Li *et al.*, 2013; Gardner *et al.*, 2015; Xu *et al.*, 2017). In concrete, fly ash has several functions as the concrete ages. In the early age stage, fly ash can act have a physical effect in that it fills up spaces in the microstructure of the concrete and it is also involved in the formation of ettringite. In the long term, they mainly participate in the hydration reaction in the form of silicon-aluminum binders (Shi *et al.*, 2006). At a later age, fly ash has two effects: it enhances the cohesion between molecules within the particle structure, and also absorbs the $Ca(OH)_2$, reducing its effect (Kolias *et al.*, 2005; Brostow *et al.*, 2016). However, Most of the molecules of the fly ash remain un-reacted even after a long period of curing, so fly ash may also be considered as a composite material with the ash particles serving as reactive micro-aggregates (Nadesan *et al.*, 2018). Structurally, fly ash is composed of lots of fine spherical micro-spheres, which are large glassy particles existing in a crystalline internal structure of fly ash. Due to density difference, the internal molecules of fly ash which are also called micro-beads or micro-spheres, are classified as sinking beads and floating beads (Li *et al.*, 2014). These micro-spheres are obtained from pulverized fuel ash (also called pulverized fly ash in some countries).

In the past decade, ultra-fine reactive fly ash (URFA) having very fine particles have been extracted by processing conventional fly ash, and it is becoming increasingly popular in the construction industry (Bagheri *et al.*, 2013). These fine particles often have a similar chemical composition with the conventional fly ash, but it has reduced surface area per particle. Recent research has shown that URFA exhibited better pozzolanic activity and more desirable performance in concrete than normal fly ash (Elsayed *et al.*, 2011; Duan *et al.*, 2018; Han *et al.*, 2019). When heated, micro-spheres heat up and crackle until they burst at about 260℃; their shells start to splinter at about 1100℃ and finally collapse at about 1300℃. The superfine particles obtained can then be used to partially replace Portland cement in cementing material systems and their particulate structures. This study aims to determine its suitability as a pozzolanic additive to improve the performance of cement-based materials.

2 Experiments

2.1 Materials

Type I Portland cement was used in this study and it had a specific gravity of 3.15 and fineness of 3310 cm^2/g. The fine aggregates are natural river sand, it has an SSD specific gravity of 2.69, an absorption of 1.45% and a fineness modulus of 2.73. The specific gravity and specific surface area of silica fume is 2.20 and 22500 m^2/kg, respectively. Silica fume having an average content of 94.1% silicon dioxide was used in powder form. URFA was provided by TRIAXIS Corporation from a power plant in Inner Mongolia. The specific gravity and specific surface area of URFA is 2.20 and 3380 m^2/kg, respectively. URFA has an average content of 49.11% silicon dioxide, 28.07% aluminum oxide and 8.84% calcium oxide.

The SEM photo of URFA particles is shown in Fig. 1 and the average particle size was between 0.1 µm to 10 µm.

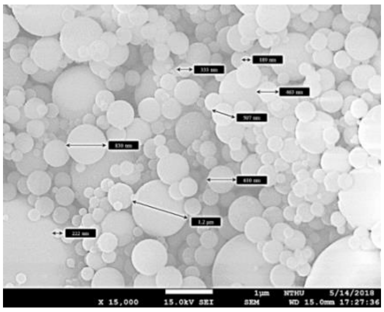


Figure 1. SEM photo of URFA.

2.2 Mix Design and Test Methods

According to the ASTM C109 specification, the water/cementitious ratio (w/c) of the mortar specimens was kept constant at 0.45, while the mass ratio of the cementitious /fine aggregates was 1: 2.75. Table 1 lists the mix designs for all mixes. The specimens were numbered using the letters and numbers to indicate the kind of replaced materials and dosage of the replaced materials. OPC, F, S denotes ordinary Portland mortar, URFA and silica fume; 5 and 10 refers to specimens containing 5% and 10% replaced materials. Table 2 presents the tests performed, the dimensions of the specimens and the standards.

Table 1. Mix design (kg/m^3).

Mix no.	Water	Cement	URFA	Silica fume	Fine aggregates	SP
OPC	242.6	547.9	0	0	1506.7	4.0
F5	243.0	520.5	27.4	0	1496.6	3.6
F10	244.0	493.1	54.8	0	1486.5	2.5
S5	241.9	520.5	0	27.4	1496.6	4.7
S10	240.9	493.1	0	54.8	1486.5	5.7
F5S5	242.1	493.1	27.4	27.4	1486.5	4.5
F8S2	243.4	493.1	43.8	11.0	1486.5	3.2

Table 2. Test methods.

Test Target		Specimen Dimensions (mm)	Referenced Standard
Fresh properties	Flow test	-	ASTM C230
Mechanical properties	Compressive strength test	50 × 50 × 50	ASTM C109
Durability	Drying shrinkage test	285 × 25 × 25	ASTM C596
	Rapid chloride penetration test	ϕ100 × 50	ASTM C1202

Micro-structure observations	Mercury intrusion porosimetry test	10 × 10 × 1	ASTM D4404
	SEM observation	10 × 10 × 1	ASTM C1723

3 Results and Discussion

3.1 Flowability

The results of flow test for all mixes are summarized in Table 3. The fluidity of the mortar specimens was controlled at 110±3% using appropriate amount of superplasticizer. The results indicated that the dosages of superplasticizer had a decrease trend with the increase in the replacement of URFA due to the due to its perfect spherical shape and micro-sized particles. However, the flowability had a decrease trend with the increase in the inclusion of silica fume due to its larger surface area. The desired flow and rheological properties will determine the optimal design mix that 10% URFA in mortar specimens should be used. The combination of silica fume and URFA in mortar specimens still had great flowability and F8S2 specimens had lowest dosages of superplasticizer at the desired flow.

Table 3. Example of the construction of a table.

Mix no.	Flowability (%)	Superplasticizer dosages (wt.% of cement)
OPC	112.3	0.73
F5	111.8	0.65
F10	110.0	0.46
S5	109.8	0.85
S10	108.3	1.04
F5S5	110.8	0.82
F8S2	109.8	0.58

3.2 Compressive Strength

The results of compressive strength test for all mixes are illustrated in Figure 2. As expected, the specimens containing 10% silica fume had highest compressive strength for all ages. The strength development trend of F10 specimens was closed to that of the S5 specimens. Compared with silica fume, URFA has a much smaller specific surface area, so it can increase bulk density without excessively increasing the total solid surface area. It is able to fill the voids in cement to increase the packing density of the cementitious materials. The compressive strengths of the F5S5 specimens were higher than that of the S5 specimens and F8S2 specimens; and the compressive strengths were lower that of the S10 specimens. URFA is considered to be a good filler for increasing parking density without excessively increasing surface area. It has a particle size of micrometer-scale and is spherical in shape. It is finer than cement and ordinary fly ash. Inclusion of URFA showed improved properties in compressive strength due to the active pozzolan reaction and filling effect.

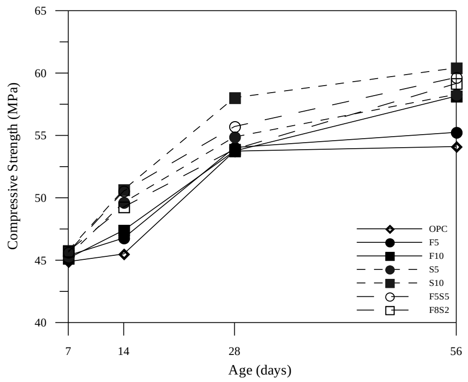


Figure 2. Compressive strength development curves.

3.3 Drying Shrinkage

The results of drying shrinkage test for all mixes are summarized in Figure 3. It indicated that drying shrinkage of the specimens containing URFA was lower than that of the specimens containing silica fume and control specimens. URFA can efficiently inhibit the dry shrinkage of mortar specimens due to the smaller specific surface area. URFA has a late hydration reaction and the dispersion effect on the cement particles can reduce the total hydration heat of the paste, and improve the drying shrinking performance.

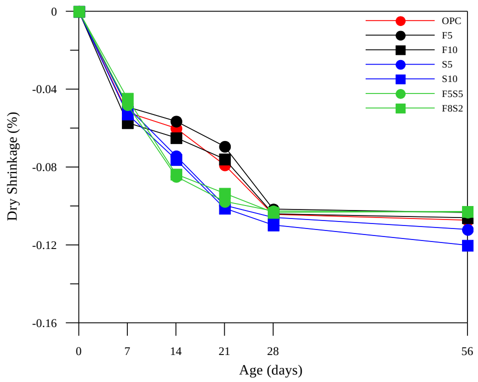


Figure 3. Dry shrinkage curves.

3.4 Chloride Penetration

The results of rapid chloride penetration test for all mixes are illustrated in Figure 4. The results indicated that the total charge passed of control specimens was higher than 10000 coulombs and the operated temperature of control specimens was higher than 90 ˚C. The test of control specimens has been stop because the temperature of the solutions should not be allowed to exceed 90 ˚C in order to avoid damage to the cell and to avoid boiling off the solutions. As expected, the specimens containing 10% silica fume had lowest total charge passed due to the finer particles. The trend of F5S5 specimens is closed to that of S5 specimens, which is due to the pore structure modification. Finer silica fume and URFA particles mixed into the mortar specimens improved the compactness through pozzolanic reactivity and pore filling effect. It may be as mainly hydrated reaction that $Ca(OH)_2$ reacted with SiO_2 or Al_2O_3 to form C-S-H or C-A-S-H colloids.

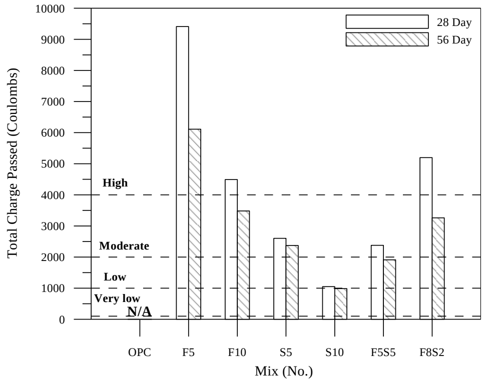


Figure 4. Total charge passed histograms.

3.5 Pore Structures

The MIP test results of the specimens containing URFA and control specimens are shown in Fig. 5. It indicated that the cumulative intrusion of specimens containing URFA significantly decreased that the control specimens. It was confirmed that the finer particles of URFA was useful to the pore structure modification, which is in agreement with the results of chloride penetration tests and compressive strength tests.

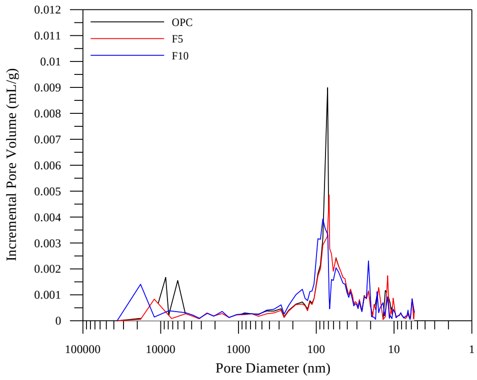
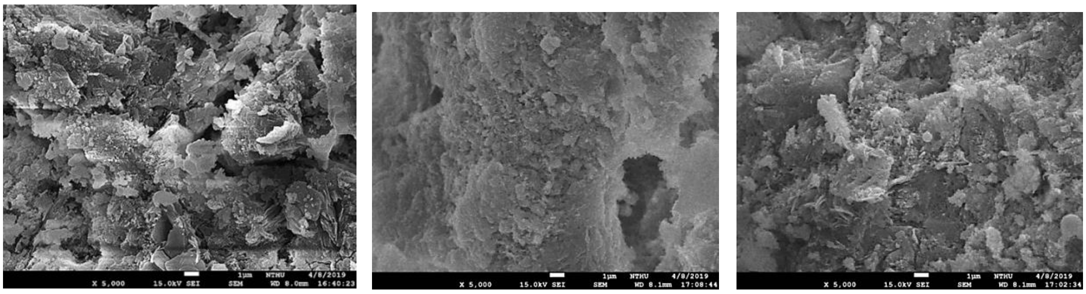


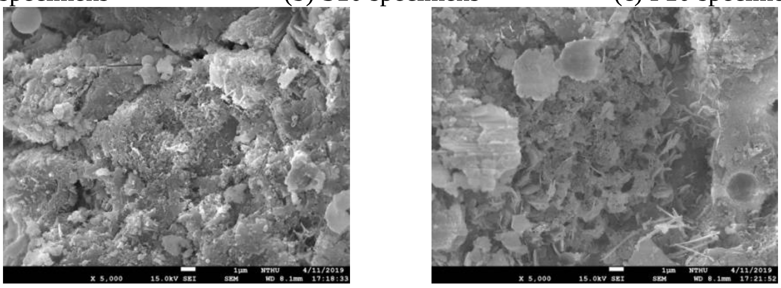
Figure 5. Intrusion pore volume versus pore diameter.

3.6 SEM Observations

It took SEM images of the various specimens at 28 days at 5000x magnification as illustrated in Figure 6. The results showed small porosity and smooth surface in the URFA or silica fume specimens than in the control specimens. Many pores in the URFA or silica fume specimens were filled with ettringite and C-S-H gel. C-S-H gel is the product of the hydrated reaction between water and tricalcium silicate or dicalcium silicate. Finer particles are needed to fill these pores. As shown, most of the pores have been filled with ettringite and C-S-H gel, which presents a dense appearance and reduces the chance of penetration of harmful substances. However, an increased amount of URFA may cause a partial reaction in the hydration process. Non-react particles of URFA can be seeing in the surface of the micro-structures. URFA is excellent cementitious filler for improving the flowability and strength of cement pastes as shown in SEM photos and it needs more curing age to keep a continued hydration reaction.



(a) control specimens (b) S10 specimens (c) F10 specimens



(d) F5S5 specimens (e) F8S2 specimens

Figure 6. SEM photos for each mixtures (x5000).

4 Conclusions

- In order to produce a balance with a desired increase in packing density and suppression of an increase in undesired surface area, URFA microspheres thinner than cement but thicker than silica fume would be a better choice.
- URFA has a particle size of micrometer scale and is spherical in shape. It is finer than cement and ordinary fly ash. The specimens containing URFA can increase the packing density so as to enhance the performance of mortar specimens. It also can significantly decrease the dry shrinkage.
- SEM observations and MIP analysis confirmed that the finer particles of URFA were useful to the pore structure modification, which is in agreement with the results of chloride penetration tests and compressive strength tests.
- Environmental friendly and helps to reduce the carbon footprint produced in cement production, since it can be used to replace cement in cement mixtures, and from a life cycle assessment perspective. It is feasible to consider URFA as a relatively CO_2 free resource.

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