Transport Properties of High Volume Fly Ash Mortar with Various Chemical Admixtures

Sen Du¹; Xianming Shi²; Yong Ge³; and Zhengxian Yang⁴

¹Graduate Research Assistant, School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, China; Department of Civil & Environmental Engineering, Washington State University, Pullman, WA 99164-2910. Email: sen.du@wsu.edu
²Associate Professor, Laboratory for Advanced & Sustainable Cementitious Materials, Department of Civil & Environmental Engineering, Washington State University, Pullman, WA 99164-2910 (corresponding author). Email: xianming.shi@wsu.edu
³Professor, School of Transportation Science and Engineering, Harbin Institute of Technology, Harbin 150090, China (corresponding author). Email: hitbm@163.com
⁴Assistant Research Professor, Laboratory of Corrosion Science & Electrochemical Engineering (CSEE), Department of Civil & Environmental Engineering, Pullman, WA 99164-2910. Email: zhengxian.yang@wsu.edu

ABSTRACT: The transport properties of concrete- and mortar are important indicators of their durability, and may be correlated to their resistance to salt scaling. This work aims to optimize the transport properties of the high volume fly ash (HVFA) mortar in which 60% (by weight) Portland cement was replaced by Class C fly ash. Ten chemical admixtures (five non-polymer and five polymers) were investigated as waterproof admixtures for HVFA mortar. The compressive strength, splitting tensile strength, water sorptivity and gas permeability of the mortar admixed with these chemical admixtures were investigated. The results showed that the non-polymer and polymer admixtures with different admixing dosages played different roles in HVFA mortar. This consequently resulted in different behavior in affecting the transport and mechanical properties of HVFA mortars.

INTRODUCTION

Fly ash is the main by-products of the coal combustion for electrical energy production. The application of increased proportion of fly ash in concrete make it a more sustainable and environmental friendly material (Celik et al. 2014), assuming there is no significant sacrifice in performance and durability of concrete. The term of high volume fly ash (HVFA) concrete is defined as a concrete in which the replacement of cement by fly ash should be at least 50% (Malhotra 2002). While many studies have demonstrated that HVFA concrete could be used in structural projects successfully, some other research showed that HVFA concrete didn’t perform well in the resistance test to cyclic freezing and thawing and salt scaling (Bouzoubaa et al. 2002; Van den Heede et al. 2013). The extent of surface scaling is greatly affected by the intrinsic capillary transport property (i.e., sorptivity and permeability) of this porous material (Liu and Hansen 2015). In order
to obtain adequate scaling resistance, mix design needs to be optimized to promote the
development of a dense and impervious concrete that resists external water penetration
(Gagné et al. 2011). Besides as an indirect indicator of the scaling resistance of concrete,
the transport property is one of the most important factors influencing the durability of
cementitious materials (Hoseini et al. 2009). Many studies reported that the HVFA
concrete featured a reduced water and gas permeability when compared to the control
concrete without fly ash (De la Varga et al. 2014; Naik et al. 1994; Van den Heede et al.
2010). However, the transport properties of HVFA mortar or concrete containing various
non-polymers and polymers have not been fully investigated.

This study examines the mechanical properties and water sorptivity of non-polymer
group (containing five different non-polymers) and polymer group (containing five
polymers) HVFA mortar. For each group, the gas permeability of six selected mortar
specimens with different water sorptivity are further tested to obtain a comprehensive
knowledge of the transport property of HVFA mortar.

EXPERIMENT

Materials

The HVFA mortars investigated in this study were prepared with ASTM Type I/II
Portland cement and a Class C fly ash. The chemical composition of the cement and fly
ash are provided in Table 1. An all-purpose siliceous sand of a fineness modulus of 2.7
was used as the fine aggregate in mortars. The high-range water-reducing agent
(HRWRA) was added into the fresh mortar to make it flowable. Two groups of HVFA
mortars were cast in this paper. Non-Polymer Group mortars contain five additives, that
is tributyl phosphate (TBP), trithanolamine (TEA), propanediol (CH₂(CH₂OH)₂,
abbreviated as PD), calcium stearate (Ca(C₁₈H₃₅O₂), abbreviated as CS), and aluminum
sulfate hexadecahydrate (Al₂(SO₄)₃×16H₂O, abbreviated as AS). Five additives added
into Polymer Group HVFA mortars are hydroxypropyl methyl cellulose (HPMC),
polyvinyl alcohol (PVA), hydroxyl terminated polysiloxane (OH-PS), ethylene-vinyl
acetate (EVA), and asphalt emulsion (AE). All the non-polymer and polymer additives
are commercially available.

| Chemical composition (wt.%) | Cement | Fly ash |
|-----------------------------|--------|---------|
| Al₂O₃                        | 3.97   | 13.77   |
| SiO₂                         | 20.44  | 23.52   |
| Fe₂O₃                        | 4.07   | 4.80    |
Statistical design of experiments

A Box-Wilson central composite design (CCD) (five factors at five levels) was employed to evaluate the influence of each mix design parameter on the compressive strength, splitting tensile strength and water sorptivity of HVFA mortars (Patel et al. 2004). A totally 26 HVFA mixtures were cast in each group. The five factors used in the study were the mass ratio of five non-polymers/polymers to binder. The total amount of binder was kept at 450 kg/m³, while the replacement of cement by fly ash was 60%. The sand to binder mass ratio was set as 1.5:1 to make the mortars more flowable with the help of the proper dosage of high range water reducing agent (HRWRA). The level range of each factor and the mixture proportions of the 26 HVFA mortars designed by following the CCD scheme in each group are detailed in Table 2, respectively. A HVFA mortar mixture was also designed without any non-polymer or polymer admixtures to act as the control mixture (named as mix #0).

| CaO   | 62.90 | 23.12 |
|-------|-------|-------|
| MgO   | 2.42  | 4.21  |
| Na₂O  | 0.37  | 6.31  |
| K₂O   | 0.43  | 0.35  |
| SO₃   | 2.6   | 5.94  |
| LOI*  | 2.7   | 1.5   |

* Loss on ignition

### Table 2. Mixture proportions of the designed HVFA mortars in both Group.

| Mix | Non-Polymer Group | Polymer Group |
|-----|-------------------|---------------|
|     | TBP, TEA, PD, CS, AS, HPMC, PVA, OH-PS, EVA, AE, |          |
|     | X₁, X₂, X₃, X₄, X₅, X₁, X₂, X₃, X₄, X₅ |          |
|     | %                 | %             |
| 1   | 0.5 0.25 1.0 1.0 0.5 | 0.25 1.5 0.5 1.5 0.0 |
| 2   | 0.8 0.40 0.8 0.4 0.2 | 0.10 2.4 0.2 2.4 2.4 |
| 3   | 1.0 0.25 0.5 1.0 0.5 | 0.25 0.0 0.5 1.5 1.5 |
| 4   | 0.5 0.50 0.5 1.0 0.5 | 0.25 1.5 0.5 1.5 1.5 |
| 5   | 0.2 0.40 0.8 1.6 0.2 | 0.40 0.6 0.8 0.6 2.4 |
| 6   | 0.8 0.10 0.8 1.6 0.2 | 0.10 0.6 0.2 0.6 0.6 |
| 7   | 0.8 0.10 0.8 0.4 0.8 | 0.25 1.5 0.5 1.5 1.5 |
| 8   | 0.5 0.25 0.5 1.0 0.5 | 0.10 2.4 0.8 2.4 0.6 |
| 9   | 0.5 0.25 0.5 2.0 0.5 | 0.25 1.5 0.5 1.5 1.5 |
| 10  | 0.8 0.40 0.2 1.6 0.2 | 0.10 2.4 0.8 0.6 2.4 |
| 11  | 0.2 0.40 0.2 1.6 0.8 | 0.25 1.5 0.5 3.0 1.5 |

66
Fabrication of mortar cylinders and test methods

All HVFA mortar mixtures were prepared in a laboratory mixer following ASTM C270 and C780 standards. The dimension of the mortar was 2″ (51 mm) D × 4″ (102 mm) H cylinder. The compressive strength (f<sub>c'</sub>) and splitting tensile strength (f<sub>s'</sub>) were tested at curing for 28 days using a SATEC compression test machine by following ASTM C109 and C496, respectively. The water sorptivity test was employed to determine the initial water sorptivity coefficient (k) of mortars in the first six hours, following ASTM C1585. The gas permeability test use liquid methanol as the gas source to determine the gas transport properties of HVFA mortars, using the method described in a reference (Han et al. 2013).

RESULTS AND DISCUSSION

Strength properties of HVFA mortars

In both group, the splitting tensile strength was reduced by admixing non-polymer or polymer admixtures when compared with the control mixture without chemical admixtures, while such reduction was not found in the compressive strength. This difference show the different role the non-polymer admixtures play in the compressive strength and splitting tensile strength in HVFA mortars, as there exist a related relationship between the compressive strength and splitting tensile strength in concrete or mortar, that is, an increase in one generally is similarly reflected in an increase in the other (Oluokun et al. 1991).
By using the Design-Expert software, the best-fit models of the mechanical properties of the mortars can be established using the following significant factors.

Non-polymer group:

\[ f'_{c} = 2.41 \times 10^{-4} + 1.672 \times 10^{-5}X_3 \]

\[ f'_{s} = 0.023 + 0.014X_4 - 0.20X_2X_4 + 0.014X_3X_5 + 4.276 \times 10^{-3}X_2^2 + 5.560 \times 10^{-3}X_3^2 + 4.945 \times 10^{-3}X_4^2 \]

Polymer group:

\[ f'_{c} = 1.378 \times 10^{-5} + 1.667 \times 10^{-6}X_4 \]

\[ f'_{s} = 15.80 + 6.31X_3X_5 \]

The response surface of the compressive and splitting tensile strength affecting by the significant factors in both group is illustrated in Fig. 1 and Fig. 2. For non-polymer group HVFA mortars, the compressive strength was mainly adversely affected by the content of propanediol (PD, \( X_3 \)). The splitting tensile strength was reduced by increasing the content of calcium stearate (CS, \( X_4 \)) in the HVFA mortars. The compressive splitting tensile strength was reduced from 40.3MPa to 37.2MPa, and 4.1MPa to 2.5MPa, with a reduction of 7.69% and 39.02%, respectively. This is due to the formation of hydrophobic layers by calcium stearate on the binder grains surfaces, during which some unhydrated and partially hydrated binder grains will also be covered. Therefore, these binder grains will be isolated from moisture, resulting in a slow hydration and thus a drop in strength (Suryavanshi and Swamy 2002). As for the polymer group HVFA mortars, a significant factor that affected the compressive strength was EVA/binder (\( X_4 \)). A reduction of 9.15% was found on compressive strength from 43.7MPa to 39.7MPa by adding the content of EVA. The polyethylene vinyl acetate (EVA) copolymer, usually as redispersible powder or latex, can be used to add into mortars or concretes to improve some properties such as fracture toughness, impermeability, bond strength, and deformability (Su et al. 1991), due to the both physical and chemical interactions between EVA and Portland cement (Betioli et al. 2009). However, these interactions only enhance the bond strength or adhesive strength, and can even have adverse effect on the compressive strength, as shown in this study. There were no significant factors for the splitting tensile strength, and this means that the splitting tensile strength of the HVFA mortar mixtures containing various polymer admixtures changed in a small range.

![Figure 1. The compressive and splitting tensile strength response surface images of Non-Polymer Group HVFA mortars.](image-url)
Figure 2. The compressive and splitting tensile strength response surface images of Polymer Group HVFA mortars.

Water sorptivity of HVFA mortars

The best-fit models of the water sorptivity of both group mortars can be obtained using the following significant factors.

Non-polymer group: 
\[ k^{-0.01} = 1.05 + 1.783 \times 10^{-3} X_1 - 3.836 \times 10^{-3} X_1 X_2 + 3.379 \times 10^{-3} X_3 X_4 \]

Polymer group: 
\[ k^{2.76} = 4.617 \times 10^{-8} - 1.166 \times 10^{-8} X_1 - 3.008 \times 10^{-8} X_3 + 2.945 \times 10^{-8} X_1 X_3 + 2.704 \times 10^{-8} X_2 X_3 + 1.923 \times 10^{-8} X_3 X_5 - 2.730 \times 10^{-8} X_4 X_5 + 9.612 \times 10^{-8} X_1^2 + 1.504 \times 10^{-8} X_3^2 \]

The water sorptivity affecting by the significant factors in both group is illustrated in the response surface images, as shown in Fig. 3. For the water sorptivity in non-polymer group, the beneficially significant factor is the content of TBP (X_1), as the water sorptivity coefficient was considerably reduced from 0.0089 mm/s\(^{1/2}\) to 0.0048 mm/s\(^{1/2}\). The performance on water sorptivity was improved by 46.07% as admixing more TBP in mixtures. TBP, well known as an effective air-detraining admixture, was found here to be also effective in reducing the water sorptivity of HVFA mortars. This is attributed to the refinement of the pore size distribution and the reduction of the porosity since the TBP can dissipate and expel the unwanted air bubbles (usually are relatively large and ineffective in providing frost resistance) from the concrete or mortar (Mather 1967). For the polymer group HVFA mortars, the content of HPMC (X_1) and OH-PS (X_3) were significantly factors affected the result of the water sorptivity test. The water sorptivity coefficient was reduced from 0.0046 mm/s\(^{1/2}\) and 0.0053 mm/s\(^{1/2}\) to 0.0038 mm/s\(^{1/2}\) and 0.0034 mm/s\(^{1/2}\), with a reduction of 17.39% and 35.85%, respectively. HPMC, usually used as the most widespread cellulose ethers used in practice as admixture, is reported can improve the mortar water retention capacity (Patural et al. 2011). The improvement effect of HPMC on the water sorptivity of the HVFA mortars may due to the refinement on the pore distribution as the HPMC films were formed between the juxtaposed air voids and along the pore wall of the single air void (Jenni et al. 2005). The adding of OH-PS
into the HVFA mortars will also lower the water sorptivity due to the hydrophobic films formed in the mixtures, as shown in Fig. 3.

**Figure 3.** The water sorptivity response surface images of non-polymer group (left) and polymer group (right) HVFA mortars.

**Gas permeability of selected HVFA mortars**

Six HVFA mortar mixtures in each group were chosen to further test their gas permeability after finishing the water sorptivity test. Mixture #3, #5, #7, #9, #13, and #17 in non-polymer group and mixture #9, #10, #14, #18, #22, and #23 in polymer group were selected considering their different water absorption performance. The six selected HVFA mortar mixtures exhibited different water sorptivity coefficient with a range from the lowest to the highest value.

Fig. 4 depicts the gas permeability coefficient of the six selected mortar mixtures in both group, as well as the control mixture. It is obviously that the gas permeability coefficient of all the six selected HVFA mortar mixtures in the non-polymer group were higher than that of the control mixture. Compared with the mixtures in non-polymer group, the mixtures in polymer group exhibited a significant reduced gas permeability coefficient ($0.2-0.6 \times 10^{-17} \text{ m}^2/\text{s}$ versus $2-6 \times 10^{-17} \text{ m}^2/\text{s}$). The polymer admixtures have been demonstrated can increase the volume of capillary pores and shift the porosity structures in the direction to smaller capillary pores (Bołtryk and Małaszkiewicz 2013). When compared with the control mixture #0, the six selected mixtures showed different performance in gas permeability since the different content of each polymer admixture added and the interaction between the admixtures.

**Figure 4.** Gas permeability coefficient of the six selected mixtures and the control mixture: non-polymer group (left), and polymer group (right).
CONCLUSIONS

This laboratory study explores the effect of ten chemical admixtures (five non-polymers and five polymers) on the mechanical properties and transport properties of the high volume fly ash (HVFA) mortars. A total of 26 HVFA mortar mixtures were designed and fabricated in both non-polymer and polymer group and the significant factors were analyzed. In both group, the splitting tensile strength was reduced by admixing non-polymer or polymer admixtures when compared with the control mixture without chemical admixtures, while such reduction was not found in the compressive strength. The water sorptivity was reduced by 46.07% and 17.39-35.85% as admixing more additives that served as significant factor in each group, respectively. For the six selected HVFA mortars with different performance in water absorption, the mixtures containing polymer admixtures exhibited a greatly improved resistance to gas permeability than the mixtures containing non-polymer admixtures (0.2-0.6 × 10^-17m^2/s versus 2-6×10^-17m^2/s on gas permeability coefficient). Further work will focus on the optimal design of the HVFA mortar, that feature the best performance on the transport properties, as well as on the mechanical properties.

ACKNOWLEDGEMENTS

The funding support was provided by the China Scholarship Council (CSC) and the USDOT Center for Environmentally Sustainable Transportation in Cold Climates (CESTiCC). The authors owe their thanks to Mr. Eric Scott Barrow at the Washington State University for his assistance in the design of the test apparatus.

REFERENCES

Betioi, A. M., Hoppe Filho, J., Cincotto, M. A., Gleize, P. J. P., and Pileggi, R. G. (2009). “Chemical interaction between EVA and Portland cement hydration at early-age.” Construction and Building Materials, 23(11), 3332–3336.

Boltryk, M., and Małaszkiewicz, D. (2013). “Application of anionic asphalt emulsion as an admixture for concrete.” Construction and Building Materials, 40, 556–565.

Bouzoubaa, N., Fournier, B., Malhotra, V. M., and Golden, D. M. (2002). “Mechanical Properties and Durability of Concrete Made with High-Volume Fly Ash Blended Cement Produced in Cement Plant.” Materials Journal, 99(6), 560–567.

Celik, K., Meral, C., Mancio, M., Mehta, P. K., and Monteiro, P. J. M. (2014). “A comparative study of self-consolidating concretes incorporating high-volume natural pozzolan or high-volume fly ash.” Construction and Building Materials, 67, 14–19.
De la Varga, I., Spragg, R. P., Di Bella, C., Castro, J., Bentz, D. P., and Weiss, J. (2014). “Fluid transport in high volume fly ash mixtures with and without internal curing.” *Cement and Concrete Composites*, 45, 102-110.

Gagné, R., Houehanou, E., Jolin, M., and Escaffit, P. (2011). “Study of the relationship between scaling resistance and sorptivity of concrete.” *Canadian Journal of Civil Engineering*, 38(11), 1238-1248.

Han, B., Yang, Z., Shi, X., and Yu, X. (2013). “Transport Properties of Carbon-Nanotube/Cement Composites.” *Journal of Materials Engineering and Performance*, 22(1), 184–189.

Hoseini, M., Bindiganavile, V., and Bantia, N. (2009). “The effect of mechanical stress on permeability of concrete: A review.” *Cement and Concrete Composites*, 31(4), 213–220.

Jenni, A., Holzer, L., Zurbriggen, R., and Herwegh, M. (2005). “Influence of polymers on microstructure and adhesive strength of cementitious tile adhesive mortars.” *Cement and Concrete Research*, 35(1), 35–50.

Liu, Z., and Hansen, W. (2015). “Freezing characteristics of air-entrained concrete in the presence of deicing salt.” *Cement and Concrete Research*, 74, 10–18.

Malhotra, V. M. (2002). “High-Performance High-Volume Fly Ash Concrete.” *Concrete International*, 24(7), 30–34.

Mather, B. (1967). *Admixtures for Concrete*.

Naik, T. R., Singh, S. S., and Hossain, M. M. (1994). “Permeability of concrete containing large amounts of fly ash.” *Cement and Concrete Research*, 24(5), 913–922.

Oluokun, F. A., Burdette, E. G., and Deatherage, J. H. (1991). “Splitting Tensile Strength and Compressive Strength Relationships at Early Ages.” *Materials Journal*, 88(2), 115–121.

Patel, R., Hossain, K. M. A., Shehata, M., Bouzoubaa, N., and Lachemi, M. (2004). “Development of Statistical Models for Mixture Design of High-Volume Fly Ash Self-Consolidating Concrete.” *ACI Materials Journal*, 101(4), 294–302.

Patural, L., Marchal, P., Govin, A., Grosseau, P., Ruot, B., and Devè, O. (2011). “Cellulose ethers influence on water retention and consistency in cement-based mortars.” *Cement and Concrete Research*, 41(1), 46–55.

Suryavanshi, A. K., and Swamy, R. N. (2002). “Development of lightweight mixes using ceramic microspheres as fillers.” *Cement and Concrete Research*, 32(11), 1783–1789.

Su, Z., Bijen, J. M. J. M., and Larbi, J. A. (1991). “Influence of polymer modification on the hydration of portland cement.” *Cement and Concrete Research*, 21(4), 535–544.
Van den Heede, P., Furniere, J., and De Belie, N. (2013). “Influence of air entraining agents on deicing salt scaling resistance and transport properties of high-volume fly ash concrete.” *Cement and Concrete Composites*, 37, 293–303.

Van den Heede, P., Gruyaert, E., and De Belie, N. (2010). “Transport properties of high-volume fly ash concrete: Capillary water sorption, water sorption under vacuum and gas permeability.” *Cement and Concrete Composites*, 32(10), 749–756.