

## **PITCHSTONE FINES: A NEW INORGANIC BINDER FOR PORTLAND CEMENT-BASED CONSTRUCTION PRODUCTS**

K. VESSALAS<sup>1</sup>, A. RAY<sup>1</sup>, P. THOMAS<sup>1,2\*</sup>, P. JOYCE<sup>3</sup> and J. HAGGMAN<sup>3</sup>

<sup>1</sup>*Centre for Built Infrastructure Research, University of Technology, Sydney, PO Box 123, Broadway NSW 2007, Australia*

<sup>2</sup>*Dept. Chemistry and Forensic Sciences, University of Technology Sydney PO Box 123, Broadway NSW 2007, Australia*

<sup>3</sup>*Perlco Pty Ltd, Suite 701, Level 7, 121 Walker Street, North Sydney NSW 2060, Australia*

*\*Email: paul.thomas@uts.edu.au*

---

### **ABSTRACT**

The findings of this investigation into the performance pitchstone fines (PF) sourced from a naturally occurring pitchstone deposit in Queensland Australia as a potential pozzolanic supplementary cementitious material (SCM) are reported. 50 mm mortar cubes were prepared by replacement of 20% of the Portland cement (PC) with PF and PF blended with silica fume (SF) in a 1:1 ratio. Mortar cubes were also prepared with a 20% PC substitution level using fly ash (FA) and FA blended with SF also in a 1:1 ratio for comparison as the SCM. Control mortar cubes without PC substitution were also prepared. The compressive strength results for PF blended mortars were comparable to FA mortars, were within 75% of the control mortar at 7 and 28 days and approached the strength of the control mortar at 91 days curing. PF and FA blends containing SF produced compressive strength which surpassed the control mortar. Drying shrinkage measurements are also reported for up to 28 days storage in air. The PF mortar was found to have comparable shrinkage to the control mortar; the shrinkage of the FA mortar was found to be significantly greater. The differences were attributed to the particle shape, angularity and size resulting in greater capillary forces in the FA mortars resulting in greater shrinkage.

### **KEYWORDS:**

Pitchstone fines; fly ash; Portland cement; strength activity index; drying shrinkage.

### **INTRODUCTION**

Portland cement (PC) is the most commonly used hydraulic binder in the building and construction industry and is primarily used for its bonding action in PC-based construction products, such as concrete. The manufacture of PC, however, has a significant environmental impact through the consumption of energy (PC manufacture is energy intensive), the consumption of natural resources and the emission of carbon dioxide (CO<sub>2</sub>). PC manufacture is estimated to be responsible for between 5% to 10% of global anthropogenic CO<sub>2</sub> emissions (Worrell et al., 2001) and, with population growth and the continued economic development, the use of PC-based construction products is expanding and, hence, PC consumption and its environmental impact is increasing (Damtoft et al., 2008).

An immediate reduction in PC consumption may be achieved with the partial replacement of PC with supplementary cementitious materials (SCMs). Typical examples of SCMs include fly ash (FA), silica fume

(SF), ground granulated blast furnace slag, clay-brick fines and perlite fines (Toutanji et al., 1995; Klimesch et al., 2004; Das et al., 2006; Duran Atis et al., 2007; Erdem et al., 2007). All of these SCMs, also known as pozzolans, are siliceous or siliceous and aluminous in nature, and possess little or no cementing ability by themselves. These SCMs will, however, in finely divided form and in the presence of water, react with calcium hydroxide (CH) liberated during PC hydration at ordinary temperatures, to form calcium-silicate-hydrate (C-S-H) gels (Ravina, 1980). It is this secondary process producing strengthening phases, as curing progresses, which allows these SCMs to be effectively used as partial replacements for PC.

FA is accepted as the industry standard SCM for the partial replacement of PC. In concrete, the use of FA improves fresh properties, such as workability while the FA particles aid pore blocking minimising bleeding and permeability. For the hardened concrete, FA provides improved strength development in the long-term by secondary formation of C-S-H phases, thus, improving durability (Siddique, 2004). The use of SCMs, therefore, provides added engineering benefits when used in PC-based construction materials in addition to the reduction of PC consumption. Supplies of SCMs, however, are dwindling and as such, new and novel SCMs need to be investigated. This paper investigates the potential of pitchstone fines (PF) as a new SCM for the partial replacement of PC.

Pitchstone has a similar composition to FA and, therefore, has the potential to act as a SCM for the partial replacement of PC. Pitchstone is a naturally occurring rhyolitic, siliceous-aluminous volcanic glass with a relatively high water content of 8% that distinguishes this glassy-amorphous material from other hydrous volcanic glasses, such as perlite (Ray et al., 2007). To date pitchstone has not received significant attention to be included as a SCM; however, recent investigations by the authors have shown that pitchstone in a finely divided form can act as a pozzolan (Vessalas et al., 2008; Vessalas et al., 2009). This paper reports on the hardened properties such as compressive strength and drying shrinkage of mortars containing pitchstone fines (PF) as a partial replacement for PC. The properties of these mortars are investigated with reference to FA. In addition, as SF is known to improve hardened properties, blends of FA and PF with SF are also investigated in this study.

## EXPERIMENTAL DETAILS

In preparing the mortar mixes, the following raw materials were utilised:

- Shrinkage Limited Portland cement (PC) supplied by Blue Circle Southern Cement Pty Ltd
- Pitchstone fines (PF) supplied by Perlco Pty Ltd
- Eraring fly ash (FA) supplied by Blue Circle Southern Cement Pty Ltd
- Densified silica fume (SF) from Techcon China Pty Ltd was supplied by Xypex Pty Ltd
- Raymond Terrace single washed sand (FS) by Rocla Quarry Products Pty Ltd
- Superplasticiser Glenium 51 supplied by BASF Construction Chemicals Pty Ltd

The chemical compositions determined by x-ray fluorescence (XRF) of the raw materials used in this study are given in Table 1.

Particle size analyses (PSAs) were conducted utilising a Malvern Mastersizer S Particle Size Analyser, with water used as the suspending medium for the PF, FA and SF and 2-propanol used as the suspending medium for the PC. The results of the PSAs are given in Table 2. The typical microstructure by use of Scanning Electron Microscopy (SEM) of the PC, PF, FA and SF particles are shown in Figure 1.

Australian/New Zealand Standard (AS/NZS) 3582.3:2002 and Australian Standard (AS) 3582.1-1998 allow the classification of an amorphous silica and FA for use with PC, respectively. Following AS/NZS 3582.3:2002, PF complies with the description of naturally occurring amorphous silica. For assessing the relative strength performance of two different SCMs in mortar, these two standards are limited, as AS/NZS 3582.3:2002 refers to use of American Society for Testing and Materials (ASTM) C 1240-05 and AS 3582.1-1998 alternatively refers to AS 3583.6-1995 for comparing compressive strength. Furthermore, AS 3583.6-1995 is restrictive for comparing relative strength between PF and FA. A suitable substitute is the ASTM C 618-08a specification allowing for comparisons of relative strength in the form of strength activity

Oxides	PC (%)	PF (%)	FA (%)	SF (%)	FS (%)
SiO <sub>2</sub>	20.16	68.32	65.13	86.85	98.4
Al <sub>2</sub> O <sub>3</sub>	4.62	13.62	23.75	0.37	0.69
Fe <sub>2</sub> O <sub>3</sub>	4.56	1.27	3.38	0.89	0.11
CaO	65.35	0.97	1.92	0.68	0.02
MgO	1.06	0.16	0.49	1.65	0.02
Na <sub>2</sub> O	-	3.70	0.48	0.40	0.03
K <sub>2</sub> O	0.44	2.50	1.46	2.53	0.17
TiO <sub>2</sub>	0.28	0.07	0.92	0.04	0.15
MnO	0.16	0.04	0.07	0.11	-
P <sub>2</sub> O <sub>5</sub>	0.07	0.04	0.25	0.17	-
SO <sub>3</sub>	2.55	-	0.07	0.81	0.05
LOI	1.16	8.38	1.65	4.51	0.372

**Table 1– XRF chemical analysis of raw materials.**

Passing (µm)	PC	PF	FA	SF
10%	1.97	2.97	1.84	4.13
50%	10.45	23.86	12.25	27.10
90%	27.58	75.83	39.58	98.55

**Table 2 – Fraction of particle size less than the value listed (D10, D50 and D90) in µm**

index (SAI) between SCM blended and control PC mortars for use in concrete. The pozzolans chosen for this study, pitchstone fines (PF) and fly ash (FA) classified as naturally and artificially derived, respectively, were assessed to conform to the 45 µm particle fineness requirement stipulated in ASTM C 618-08a (Table 2).

Since the workability of the fresh mortars is an important factor in determining the hardened properties, in particular, compressive strength, a consistent flow, measured in accordance with AS 2701-2001, was set at  $55 \pm 10\%$ , which was deemed desirable for each mortar mix. Flows beyond 65% exhibited signs of the onset of bleeding and segregation, whereas mixes below 45% flow were characterised as too dry for consolidation of mortar into moulds. In order to attain a consistent flow, a polycarboxylic-ether based high-range water-reducing admixture (HRWRA), Glenium 51, was introduced in all mixes following ASTM C 1240-05. As the HRWRA is supplied as an aqueous solution, the water contents for all mixes were adjusted to compensate for the 65% fraction of water present in the HRWRA. Flows are listed in Table 3.

Proportioning of mortar mixes, shown in Table 3, were batched using a fixed cementitious material-to-sand ratio of 1:2.75 and fixed water-to-cementitious material ratio (w/cm) of 0.48, as an increase in w/cm has been reported to decrease compressive strength, respectively (Hover et al., 1995). With the variability in PC and SCM contents stated in test method AS 3583.6-1995, fixed mix design quantities were proportioned following the guidelines stipulated in ASTM C 311-07. Preparation of mixes were carried out in accordance with AS 2350.12-2006, with the inclusion of an additional step requiring pozzolan additions to be pre-mixed with water for 30 seconds at  $140 \pm 5$  revolutions/min prior to introducing PC.

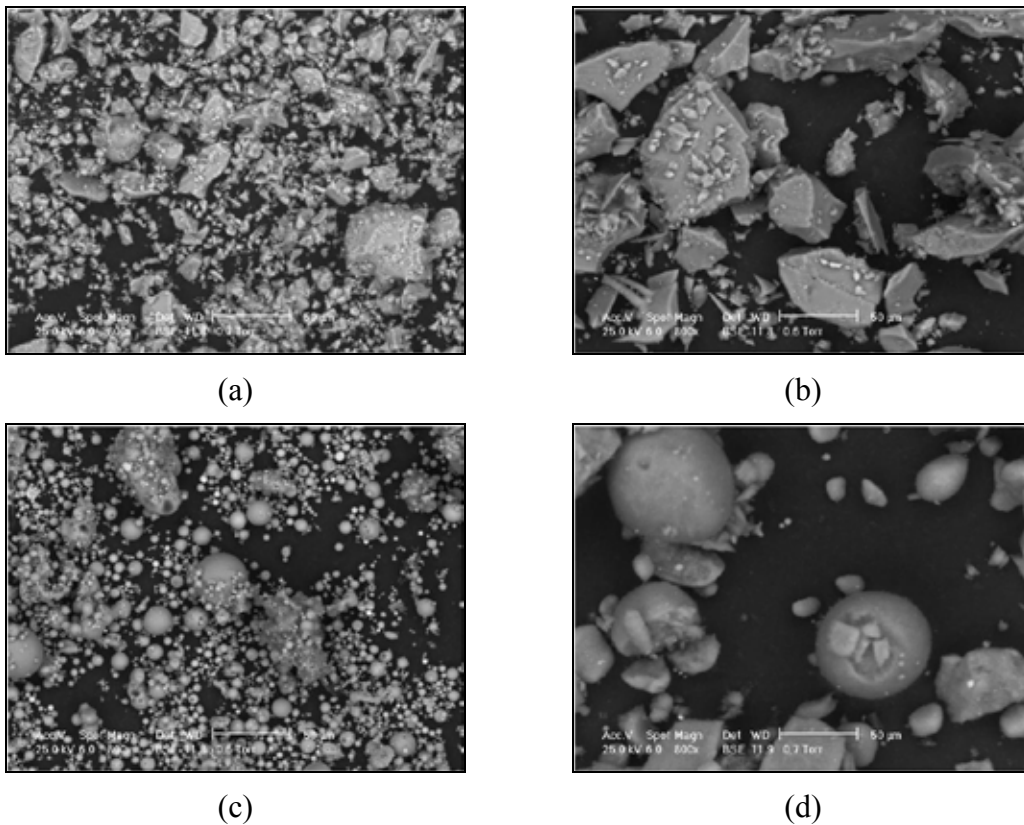


Figure 1 – SEM micrographs of (a) PC, (b) PF, (c) FA and (d) SF (width of view is 300  $\mu$ m).

Mix Designation	PC (g)	PF (g)	FA (g)	SF (g)	FS (g)	W (g)	G 51 (mL)	flow (%)
100PCwc	500.0	0.0	0.0	0.0	1375.0	241.6	0.6	54
20PFwcm	400.0	100.0	0.0	0.0	1375.0	241.1	1.4	53
20FAwcm	400.0	0.0	100.0	100.0	1375.0	241.9	0.2	50
20PFSFwcm	400.0	50.0	0.0	50.0	1375.0	240.6	2.2	57
20FASFwcm	400.0	0.0	50.0	50.0	1375.0	241.1	1.4	56

Table 3 – Mix design proportions of mortar specimens

Based on the prescribed methodology, five mortar mixes using a 20% partial substitution level replacing PC were prepared, as follows:

1. 100% PC control (100PCwc)
2. 20% PF (20PFwcm)
3. 20% FA (20FAwcm)
4. 10% PF and 10% SF (20PFSFwcm)
5. 10% FA and 10% SF (20FASFwcm)

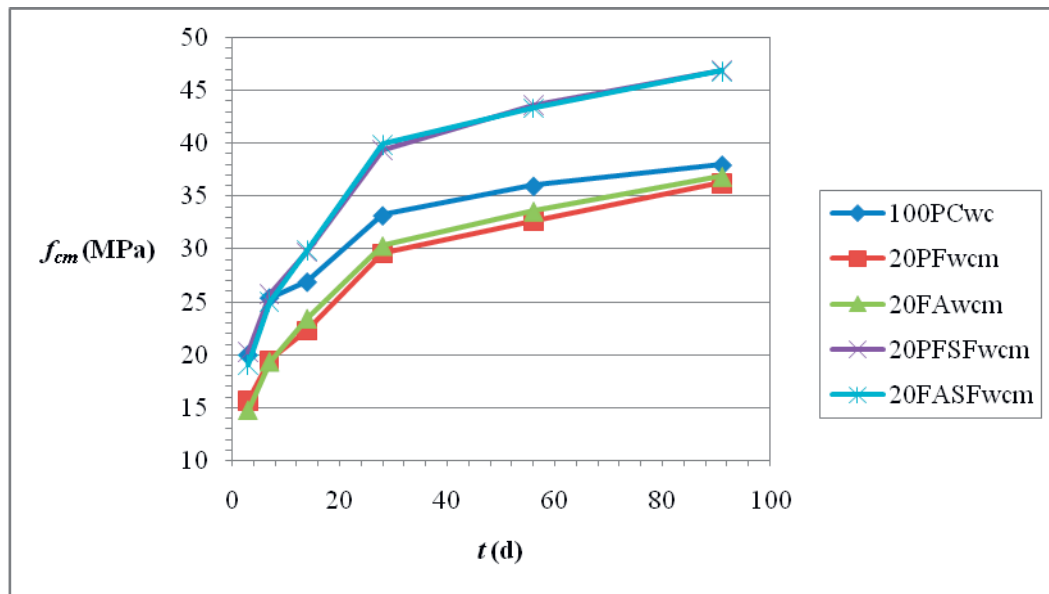


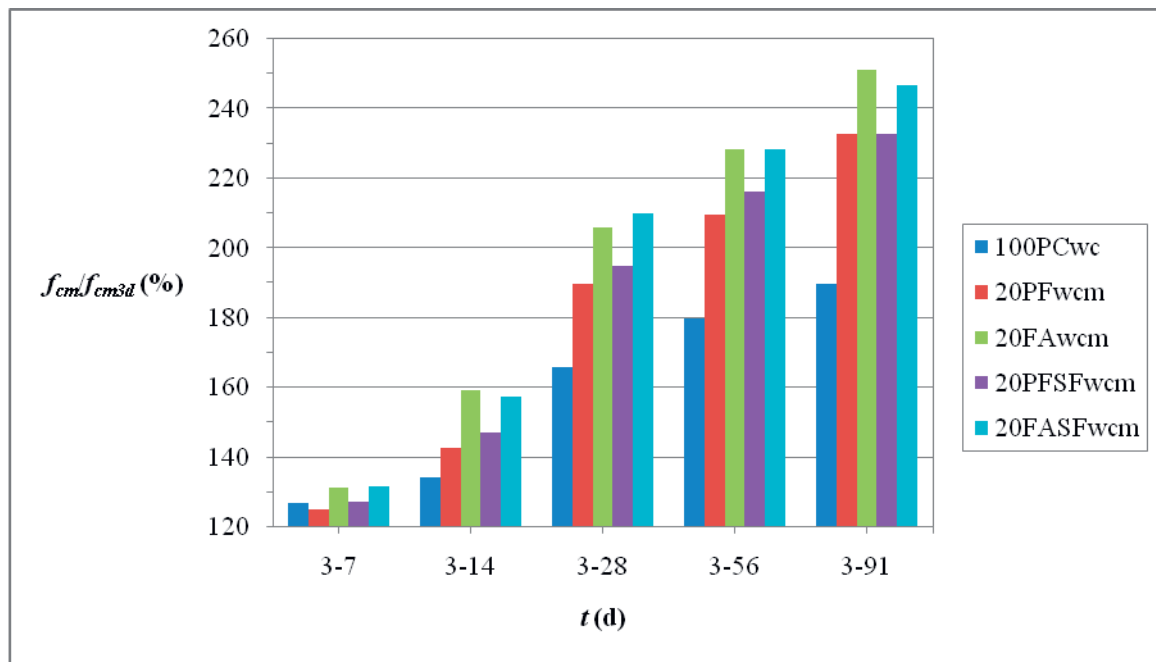
Figure 2 – Compressive strength ( $f_{cm}$ ) versus age (d = 24 h) for each mortar type after standard curing regime in water

Three mortar cubes representative of each mix were moulded in compliance with ASTM C 109/ C 109M-08 using the hand-tamping compaction technique for consolidation of mortar. Moulded 50-mm cubes were cured initially for 24 hours in a moist environment and then placed in lime-saturated water. After 3, 7, 14, 28, 56, and 91 days curing in lime-saturated water, the cube specimens were removed for compressive strength testing. Compressive strength was determined using a calibrated Tinius Olsen Super L 600 kN hydraulic universal testing machine. Prior to testing at 3, 7, 14, 28, 56 and 91 days ageing, the cube dimensions were measured to an accuracy of 0.1 mm using electronic vernier callipers.

The drying shrinkage was evaluated for all five mortar types. At the completion of 7 days water ageing, storage periods of 7, 14, and 28 days in air were selected for assessing the extent of drying shrinkage relative to 0 day length (taken at 7 days water ageing). Drying shrinkage was determined in accordance with the requirements stipulated in AS 2350.13-2006, ASTM C 311-07 and ASTM C 157/C 157M-08 test methods, using mortar bar specimens of dimensions 120 × 16 × 16 mm. Length measurements, to the nearest 0.001 mm were recorded after 0, 7, 14 and 28 days air storage using a Mitutoyo Digimatic caliper (Model ID C11) and a length comparator manufactured by CIVILAB Australia.

## RESULTS AND DISCUSSION

Curing in lime-saturated water was carried out to assess the pozzolanic activity of the SCMs relative to the compressive strength of the control mortar with increasing age (Figure 2). The strength of all the mortars were observed to increase with increasing age. Although the strength of the FA and PF substituted mortars were observed to be lower than that of the control mortar, a similar trend in the development of strength was noted with increasing age, indicating similar pozzolanic activity for the PF and FA. The strength of the PF mortar cubes was, however, found to be slightly lower than that of the equivalent FA mortar cubes. It is likely that this strength difference is due to the relative particle fineness; PF has a coarser particle size distribution than the FA (Table 2). The larger particle size may be related to a reduced reactivity and, hence, a slightly lower strength. The spherical shape of the FA particles in mortar may also be responsible for improving the packing density of cement particles in the cementing structure, resulting in the occurrence of



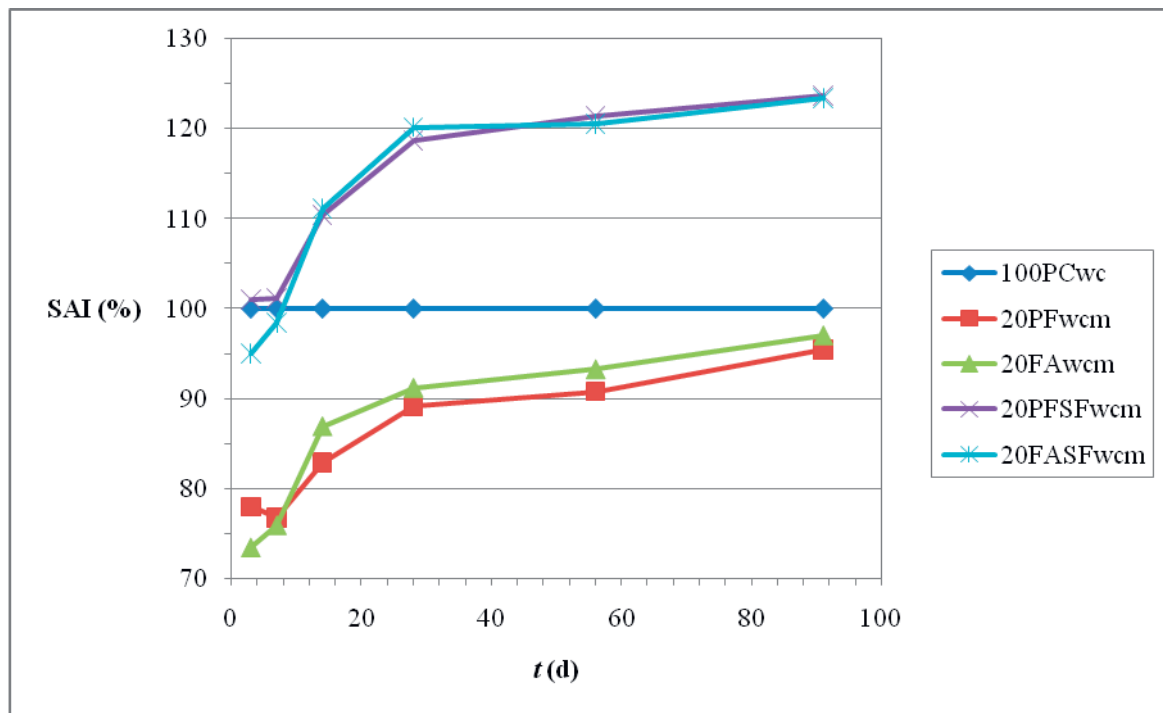
**Figure 3 – Strength relative to 3 day strength (%) versus time intervals (d = 24 h) for each mortar type after standard curing regime in water**

fewer voids leading to improved strength (Chindapasirt et al., 2004). The strength of the SF blended mortars were observed to be significantly greater than the control mortar and both the FA and PF-SF blended mortars produced very similar compressive strength indicating that the strength was provided by the reactivity of the SF in the mortar.

With increasing age, the strength of the FA and PF mortars approached that of the control mortar. The development of strength in the long term may be attributed to the pozzolanic reaction between the PF and FA and CH liberated by the hydration of PC to produce C-S-H strengthening phases. As the pozzolanic reaction of the SCM with CH liberated by the hydration of PC is a relatively slow process, the delayed effect of the pozzolanic reaction may be demonstrated by measurement of the relative increase in strength with age. The strength normalised to the 3 day strength is shown in Figure 3. The control mortar has the lowest relative strength increase as a significant degree of strength development occurs on rapid hydration of the tricalcium silicate ( $C_3S$ ) component in PC in the first 3 days. Strength continues to develop with age as the  $C_3S$  continues to hydrate and the slower hydration after 28 days of the dicalcium silicate ( $C_2S$ ) in the PC occurs. For all SCM mortars up to 7 days ageing, a similar relative increase in strength is observed. Beyond 7 days, the relative increase in strength for the SCM mortars are all higher than the control with the greatest increase observed for the FA mortar, although the PF mortar is not far behind. These increasing degrees of relative strength increase are indicative of the slow pozzolanic reaction aiding the development of strengthening C-S-H phases with time. The SF blended SCM additions are also observed to increase at a similar rate for the later ages. This indicates that the strength provided by the SF occurs in the early part of the curing while later strength results predominantly from the delayed pozzolanicity of the PF and FA.

The development of strength with age through the pozzolanic activity of the SCMs is exemplified by the Strength Activity Index (SAI) data shown in Figure 4 measured in accordance with ASTM C 618-08a specifications. SAI is a relative measure of the strength of a SCM mortar expressed as a percentage of the strength of the PC control mortar at the same age (the control SAI at each age is 100% by definition). The SAIs show that the strength of the SCM mortars approach that of the control mortar at 91 days ageing for the





**Figure 4 – Strength activity index (SAI) versus ageing time (d = 24 h) for each mortar type after standard curing regime in water**

20% FA and PF additions again showing the delayed pozzolanic reaction. Although both the SAIs of the PF and FA blended with SF mortars significantly surpass 100% SAI at 91 days ageing, both of these blends also show developing strength with age, at a greater rate than the control mortar, once again showing the effect of the delayed pozzolanic reaction.

The ASTM C 618-08a specification is set out to classify a SCM with the stipulation that a SCM is pozzolanic if the SAI at 7 or 28 days is at least 75%. All SCMs studied in this investigation have SAIs of greater than 75% at both 7 and 28 days. As such, both PF and FA may be classified as pozzolanic SCMs according to this standard.

For SCMs to be viable, the hardened PC-based construction product must also be durable. A potentially significant problem for PC-based construction products is drying shrinkage that can lead to catastrophic failure of the bonded component from the initiation of cracking and consequent application of load. Drying shrinkage is mainly associated with the removal of water primarily through evaporation from capillary pores. The size and number of these capillary pores is strongly dependent on the SCM used and its influence of particle shape, angularity and size on the cementing microstructure. The micrographs of SCMs imaged in Figure 1 show significant differences between shape and angularity of particles. From these variations, differences in drying shrinkage of these SCM mortars are expected and are shown in Figure 5. Surprisingly, the FA and FA-SF mortars showed the greatest amount of shrinkage. The PF mortars showed comparable shrinkage to the PC control mortar. The PF-SF mortar showed an intermediate degree of shrinkage. These results can be explained in terms of the particle size and shape (Tangpagasit et al., 2005). The large angular particles of PF result in large pores, which are greater in size than typical capillary pores reducing the tendency towards shrinkage associated with capillary action. The FA on the other hand, has small spherical particles that pack well producing more smaller capillary pores that result in greater shrinkage. The SF further increases the proportion of capillary pores resulting in even greater shrinkage.

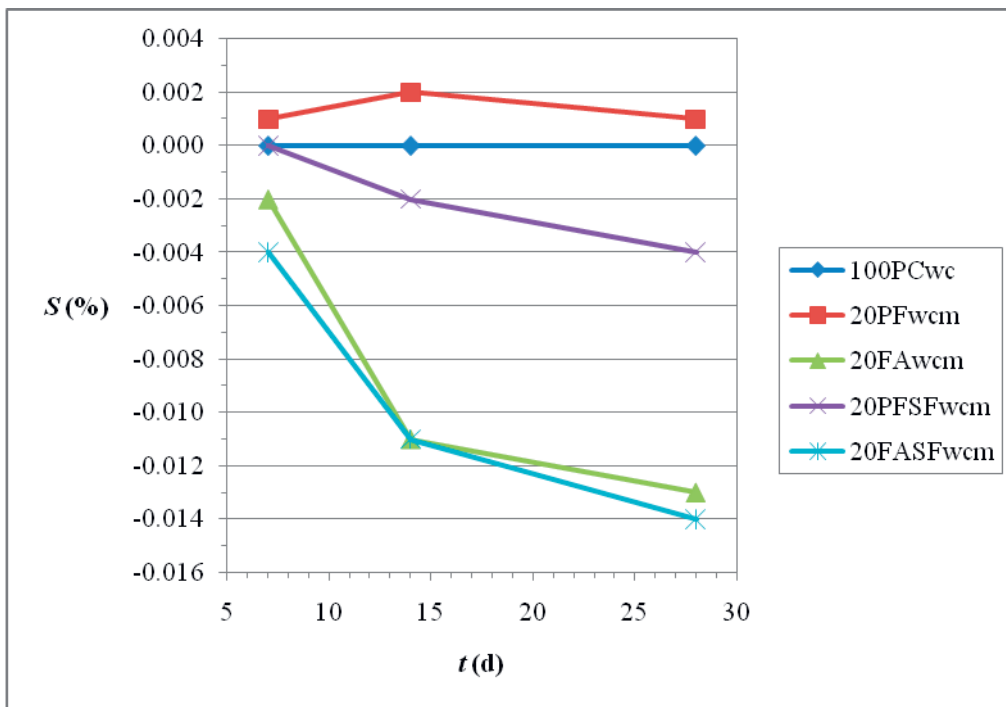


Figure 5 – Drying shrinkage ( $S$ ) versus air storage time ( $d = 24$  h) for each mortar type

## CONCLUSIONS

PF and FA mortars displayed comparable compressive strength. The PF, therefore, has demonstrated its potential for use as a SCM. At the 20% substitution levels investigated in this study, both PF and FA SCM mortars produced compressive strength within the 75% limit (both attained SAIs of greater than 75%) of the control mortar at 7 days ageing and beyond fitting into the ASTM classification of these SCMs as pozzolanic. Therefore, PF qualifies as a pozzolanic SCM. Blending the FA and the PF with the SF produced significant increases in strength, as SF is highly pozzolanic.

The drying shrinkage of the PF mortar was found to be comparable to that of the control PC mortar while that of the FA mortar and the FA-SF and PF-SF mortars demonstrated increased shrinkage. This difference was attributed to the difference in particle size shape and angularity. FA (and SF), which contain particles that are more spherical, produced greater packing and, hence, more capillary pores in the mortars resulting in increased drying shrinkage.

Overall, PF has performed as well as FA in strength terms and showed its ability to resist drying shrinkage, at least over the 28 day air storage period studied. These positive results show that PF should be classified as a new pozzolanic SCM.

## ACKNOWLEDGMENTS

The authors would like to thank the University of Technology, Sydney (UTS) Challenge Grants Scheme, Centre for Built Infrastructure Research and Perlco Pty Limited for funding this research. For their experimental assistance, the authors would further like to thank Padraic Joyce and Ken Vo.



**REFERENCES**

- Chindaprasirt, P., Homwuttiwong, S. and Sirivivatnanon, V. 2004. "Influence of fly ash fineness on strength, drying shrinkage and sulfate resistance of blended cement mortar". *Cement and Concrete Research* 34(7) 1087-1092.
- Damtoft, J. S., Lukasik, J., Herfort, D., Sorrentino, D. and Gartner, E. M. 2008. "Sustainable development and climate change initiatives". *Cement and Concrete Research* 38(2) 115-127.
- Das, S. K. and Yudhbir 2006. "A simplified model for prediction of pozzolanic characteristics of fly ash, based on chemical composition". *Cement and Concrete Research* 36(10) 1827-1832.
- Duran Atis, C. and Bilim, C. 2007. "Wet and dry cured compressive strength of concrete containing ground granulated blast-furnace slag". *Building and Environment* 42(8) 3060-3065.
- Erdem, T. K., Meral, C., Tokyay, M. and Erdogan, T. Y. 2007. "Use of perlite as a pozzolanic addition in producing blended cements". *Cement and Concrete Composites* 29(1) 13-21.
- Hover, K. and Stokes, T. 1995. "Making 'cents' out of the water-cement ratio". *Concrete International* 17(5) 52-54.
- Klimesch, D., Gutovic, M. and Ray, A. 2004. "Use of DTA-TG in the evaluation of autoclaved cement-based systems: Part I. Cement-brick waste blends". *Journal of Thermal Analysis and Calorimetry* 75(1) 197-204.
- Ravina, D. 1980. "Optimized determination of PFA (fly ash) fineness with reference to pozzolanic activity". *Cement and Concrete Research* 10(4) 573-580.
- Ray, A., Sriravindrarah, R., Guerbois, J. P., Thomas, P. S., Border, S., Ray, H. N., Haggman, J. and Joyce, P. 2007. "Evaluation of waste perlite fines in the production of construction materials". *Journal of Thermal Analysis and Calorimetry* 88(1) 279-283.
- Siddique, R. 2004. "Performance characteristics of high-volume Class F fly ash concrete". *Cement and Concrete Research* 34(3) 487-493.
- Tangpagasit, J., Cheerarot, R., Jaturapitakkul, C. and Kiattikomol, K. 2005. "Packing effect and pozzolanic reaction of fly ash in mortar". *Cement and Concrete Research* 35(6) 1145-1151.
- Toutanji, H. A. and El-Korchi, T. 1995. "The influence of silica fume on the compressive strength of cement paste and mortar". *Cement and Concrete Research* 25(7) 1591-1602.
- Vessalas, K., Ray, A. S., Thomas, P. S., Joyce, P. and Haggman, J. 2008. "Characterisation of Portland Cement Blended with Pitchstone Fines Aiding Carbon Dioxide Emission Reduction". *In* "International Congress for Applied Mineralogy 2008 Conference Proceedings", Brisbane, Queensland, Australia.
- Vessalas, K., Thomas, P., Ray, A., Guerbois, J., Joyce, P. and Haggman, J. 2009. "Pozzolanic reactivity of the supplementary cementitious material pitchstone fines by thermogravimetric analysis". *Journal of Thermal Analysis and Calorimetry* 97(1) 71-76.
- Worrell, E., Price, L., Martin, N., Hendriks, C. and Meida, L. O. 2001. "Carbon dioxide emissions from the global cement industry". *Annual Review of Energy and the Environment* 26(1) 303-329.