CHARACTERISATION OF PORTLAND CEMENT BLENDED WITH PITCHSTONE FINES AIDING CARBON DIOXIDE EMISSION REDUCTION

K. VESSALAS[1], A. S. RAY[1*], P. S. THOMAS[1],
P. JOYCE[2] and J. HAGGMAN[2]

[1]*Centre for Built Infrastructure Research,*
University of Technology, Sydney
PO Box 123, Broadway NSW 2007, Australia
[2]*Perlco Pty Ltd,*
Suite 701, Level 7, 121 Walker Street,
North Sydney NSW 2060, Australia
**Email: a.ray@uts.edu.au*
**Facsimile: +61 2 9514 1460*

ABSTRACT

Climate change and global warming present a significant challenge as unstainable levels of greenhouse gas emissions arising from human induced activities continue to be emitted. The cement industry is responsible for between 5 and 10% of annual world carbon dioxide emissions; most arising from the manufacture of Portland cement (PC). An effective way of reducing emissions is by incorporating supplementary cementitious materials (SCMs) as partial PC replacements. SCMs are silicate or aluminosilicate based pozzolanic materials which, in finely divided form, combine with water and calcium hydroxide (lime), liberated by cement hydration, to form compounds exhibiting cementitious properties. Pitchstone is such an aluminosilicate and has the potential to act as an effective pozzolan in the partial replacement of PC.

In North Queensland, Australia, a vast deposit of pitchstone is mined and processed for expandable perlite aggregate. During the classification stage of the excavated natural material, pitchstone fines (PF) less than 0.5 mm in size are generated, which currently have no commercial significance since only the coarser grade is used in expandable perlite applications. This study evaluates the waste PF as a viable, ecofriendly pozzolan for the partial replacement of PC. The reactivity of the PF is compared to fly ash (FA), using the pozzolanic compressive strength activity index (SAI) after 7, 28, and 91 days ageing at 20% and 40% PC substitutions. PF was found to be comparable to FA as a pozzolan at 20% PC substitution at all ages tested. However, for the 40% substitution blends significant strength was only achieved at 91 days ageing for the FA blend. The pozzolanic reactivity was also investigated using thermogravimetric analysis to determine the degree of free lime present after 91 days. In all cases where an SCM was added, the free lime was observed to be consumed with increasing age.

KEYWORDS

Pitchstone fines, perlite, fly ash, Portland cement, pozzolan, strength activity index

INTRODUCTION

Increasing worldwide concern over the greenhouse effect responsible for the onset of global warming, climate change and altered weather patterns has intensified in recent years. This has resulted in a greater push in developing environmentally responsible solutions for controlling and restricting the amount of emissions generated. The manufacture of Portland cement (PC) is known to be a significant contributor to green house gas emissions with between 5 to 10% of global anthropogenic CO_2 emissions estimated to originate during cement manufacture (Worrell et al., 2001). For each tonne of cement produced, an equivalent amount of CO_2 is released.

For cement based building products, one method for decreasing greenhouse gas emissions is by reducing the amount of PC consumed. This can be achieved through the partial replacement of PC with supplementary cementitious materials (SCMs) which include natural and artificially derived materials, in particular, by-product materials. A SCM, otherwise known as a pozzolan, is a siliceous or siliceous-aluminous material, possessing little or no cementitious attributes, but will in finely divided form and in the presence of water, chemically react with calcium hydroxide (CH) which is liberated during PC hydration at ordinary temperatures to form compounds possessing cementitious properties (ASTM C 125-07, 2007).

Pozzolans, as partial PC replacements, are also important to the construction industry as they improve fresh and hardened-state properties, enhance workability, reduce permeability and heat of hydration, improve durability resistance and increase ultimate strength development (Uzal, Turanli and Mehta, 2007). In PC-SCM blended systems, the evaluation of pozzolanic silica-rich industrial by-products including pulverised fuel (fly) ash (FA), silica fume, ground granulated blast furnace slag, clay-brick waste and perlite for use as SCMs, have been investigated with positive outcomes reported (Das and Yudhbir, 2006, Detwiler and Mehta, 1989, Duran Atis and Bilim, 2007, Fraay, Bijen and de Haan, 1989, O'Farrell, Sabir and Wild, 2006, Yu, Ou and Lee, 2003). In the this paper, the naturally occurring, glassy, aluminosilicate material, pitchstone is investigated as a potential SCM. Pitchstone is a rhyolitic volcanic glass which has similar composition to perlite and obsidian. The main distinction is in the water content where obsidian contains less than 2%, perlite between 2% and 5% and pitchstone greater than 5% water (Sodeyama et al., 1999). In this group of rhyolitic glasses, perlite is unique due to its ability to expand to 20 times its volume upon heating and, hence, can be transformed into an ultra-low bulk-density material. These properties make expanded perlite ideal for commercial applications, such as construction, chemical, horticultural and petrochemical industries.

In Far North Queensland, Australia, a large pitchstone deposit, located in the Nychum district near the town of Chillagoe, approximately 200 km west of Cairns, has the potential to provide in excess of 100 million tonnes of high quality mined pitchstone. This vast deposit of pitchstone is mined and processed for expandable perlite aggregate. During the crushing and classification stage, 30% of the pitchstone material is generated as pitchstone fines (PF) with a particle size of less than 500-µm. These PF currently have no commercial significance since only the coarser grade is used in expandable perlite applications. The by-product PF is, thus, stockpiled on-site as a waste material.

Rhyolitic glasses have yet to be fully explored as SCMs for inclusion in cement-based building products, however, reported data has demonstrated the potential for pozzolanic reactivity of these aluminosilicate glasses. Yu, Ou and Lee (2003), investigating the potential of perlite as an SCM, demonstrated significant pozzolanic reactivity and improvement in compressive strengths relative to control specimens at 91-days ageing for PC replacement amounts ranging from 10 to 40%. Erdem et al. (2007), in the evaluation of perlite powder particle fineness, blended perlite with PC to form mortar samples and reported that the compressive strengths for finer grade perlites at 20 and 30% replacements approached control specimens at 91-days ageing. Investigations by Ray et al. (2007) into waste perlite fines reported that, at 10% PC replacement and at 28-days ageing, compressive strengths almost equivalent to control were achievable, surpassing the equivalent reported performance of FA substitutions. Continuing investigations by Vessalas et al. (2008 a, 2008 b) into waste pitchstone fines (PF) have demonstrated that 10 and 20% of PC substitutions at 7 and 28-days ageing were found to conform to American Society for Testing and Materials (ASTM) standard test method strength activity index (SAI) measurements, for classification as a pozzolan (ASTM C 311-05).

In order to quantify the effectiveness of these SCM additives, the degree of pozzolanic reactivity (pozzolanicity) of each SCM must be assessed. In this study, the pozzolanic activity is assessed by evaluating the extent of the reaction between the CH, liberated during PC hydration, and the active amorphous silica or aluminosilicate SCM during the formation of the C-S-H strengthening phases. This can be achieved by utilising physical and chemical monitoring methods to characterise levels of pozzolanicity applicable to hardened, blended PC-SCM product. The most notable of the physical testing methods is the ASTM SAI testing method for evaluating pozzolanicity (ASTM C 311-05). The method relies on the measurement of compressive strength to assess the degree of reactivity. At a given age, the compressive strength obtained for the blended PC-SCM product is compared to that of the control. For any potential SCM to be classified as a pozzolan, the SAI must be greater than 75% at either 7 or 28-days ageing (i.e. the hydraulic strength of the blended pozzolan cement must not be less than 75% of the control's strength).

In addition to the measurement of SAI of PF blended cements, equivalent FA blended cements were also prepared and characterised in this study. FA is the most widely utilised pozzolan for improving numerous fresh and hardened-state properties and is accepted as an industry standard SCM. Although FA is an artificially derived pozzolan, captured as the inorganic by-product in the combustion gases generated from coal-thermal power stations, it has a number of similarities with PF as both FA and PF are amorphous aluminosilicate materials.

Simultaneous differential thermal (SDT) analysis represents another effective tool for assessing the amount of pozzolanicity applicable to a SCM. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) are useful for analysing the amount of CH and calcium carbonate ($CaCO_3$) present. Quantification of the proportion of liberated CH is determined from the mass loss recorded with increasing temperature for the de-hydroxylation of CH (440 to 580°C) and de-carbonation of $CaCO_3$ (580 to 1000°C). The measurement of the degree of consumption of the free CH (lime) by the pozzolan present represents a means of determining the pozzolanicity of the SCM and its ability to form C-S-H strengthening phases (Roszczynialski, 2002, Bhatty and Reid, 1985, Moropoulou, Bakolas and Aggelakopoulou, 2004).

EXPERIMENTAL DETAILS

Graded pitchstone fines (PF) and fly ash (FA) meeting ASTM grading requirements were selected as the source of pozzolans under examination. In preparing mortar mixtures with PC and fine sand (A) for this study, the following raw material ingredients were utilised:

1. Shrinkage limited Portland cement (Blue Circle Southern Cement Pty Ltd)
2. Graded pitchstone fines (Perlco Pty Ltd)
3. Eraring fly ash (Blue Circle Southern Cement Pty Ltd)
4. Raymond Terrace single washed sand (Rocla Quarry Products Pty Ltd)

To obtain optimal workability for all mixtures, Glenium 51 superplasticiser (BASF Construction Chemicals Pty Ltd), a high range water reducing admixture (HRWRA), was incorporated in order to achieve equivalent mortar flow.

Full details of the experimental program adopted, outlining procedures and methods of testing compressive strengths of mortar cubes at 7, 28 and 91-days ageing for control, 20% and 40% PF and FA substitutions, are provided in Vessalas et al. (2008c). Corresponding flow, density data and compressive strengths for all mortar mixtures are reported and discussed in Vessalas et al. (2008c), with this investigation examining pozzolanicity levels of low and high volume PF and FA additions by SAI measurements and SDT thermograms.

Chemical compositions, determined by x-ray fluorescence (XRF) analysis, of the raw materials used in this study are given in Table 1 and the pozzolan particle size profile grading of PF and FA are listed in Table 2. The mortar mixture design proportions, shown in Table 3, were batched with cementitious material-to-sand and water-to-cementitious material (w/cm) ratios fixed at 1:2.75 and 0.48, respectively, as any increase or decrease in the latter ratio has been reported to decrease or increase compressive strengths, respectively (Hover and Stokes, 1995).

On completing strength testing of the mortar cubes, at 7, 28 and 91-days ageing, fractured fragments were collected and placed inside sealed air-tight bags and stored in a freezer, set at approximately -10°C, to arrest ongoing hydration until the time of pulverising. Approximately 50 grams of each mixture type, sampled from internal fractured surface regions of the cubes, were reduced in size initially utilising a hammer followed by pulverising for 1 minute in a TEMA T100 vibrating ring mill. Homogenous representatives of the resulting air-dried ultra-fine powdered samples were collected and placed in stoppered glass jars inside a desiccator under controlled storage laboratory conditions of 22°C, until simultaneous differential thermal (SDT) analysis was carried out. Approximately 25 milligrams of samples were analysed by a TA Instruments SDT 2960 differential thermal and thermogravimetric analysis (DTA-TGA) analyser at a heating rate of 10°C per minute from room temperature to 1000°C with an air flow rate of 15 mL per minute.

RESULTS & DISCUSSION

Strength Activity Index (SAI)

The SAI values for all the SCM blended cements listed in Table 4 were noted to increase, progressively, with increasing maturity. For the low volume 20% SCM substitutions, a clear relationship is evident between the SAI values obtained for the $20PF_{wcm}$ and $20FA_{wcm}$ series at all ageing periods (Figure 1, Table 4). The matching SAI trend to 91-days suggests continuing pozzolanic reactivity with age and, hence, continual development of the strengthening C-S-H phases. Additionally, the $20PF_{wcm}$ and $20FA_{wcm}$ series both comply with the ASTM SAI 75% permissible limit for qualification as a pozzolan for all ageing periods tested. The early age SAI values obtained at 7-days for both the $20PF_{wcm}$ and $20FA_{wcm}$ series, in particular, are noteworthy, as passing the ASTM SAI stipulated minimum value indicates that the usage of PF substitutions at 20% PC replacement levels in concrete-based applications is feasible and directly comparable to FA, the industry accepted SCM.

The SAIs for the high volume (40%) substitutions did not fulfil the ASTM criteria for classification as a pozzolan for either SCM with the exception of the SAI value for the $40FA_{wcm}$ blended cement after 91 days ageing (although the $40PF_{wcm}$ is not far off with a SAI of 73%). Although, overall, the SAI values did not achieve the 75% limit for the 40% substitution level, the progressively increasing magnitudes of the SAI with age indicates that strength development will continue to increase. The continued increase in SAI suggests that, given further ageing time, the strengths of the 40% substitution blends would likely surpass the 75% stipulated limit for both systems.

A discernible difference in the SAI between the $40FA_{wcm}$ and $40PF_{wcm}$ blended cements was also notable. This difference in SAI for these high volume substitutions may be explained by the coarser particle size of PF in comparison to the FA (Table 2). The coarser particle size is likely to reduce reactivity and pozzolanicity and, hence, reduce the SAI. Reducing the particle size to a comparable size of the FA would likely rectify this difference in SAI values.

Simultaneous Differential Thermal (SDT) Analysis

The occurrence of de-hydroxylation of CH, from 440 to 580°C, and that of de-carbonation of $CaCO_3$, from 580 to 1000°C, allows SDT data to be used to estimate the amount of overall free lime present in the system after the hydration of the PC.

The CH and $CaCO_3$ peaks are clearly visible after 7 days of aging (Figure 2). These peaks remain in the case of the 100% PC control sample, as there is no pozzolan present for reaction with the liberated CH. For the $40PF_{wcm}$ and $40FA_{wcm}$ series, however, the SDT thermograms at 91 days show little or no evidence of peaks in these regions suggesting that the liberated lime, both as lime and carbonate, is consumed by the pozzolanic reaction with the aluminosilicates of the SCMs in the formation of the strengthening C-S-H phases.

The consumption of lime due to the pozzolanic reaction between the lime released by the hydration of the cement and the aluminosilicate SCMs up to 91-days is a further indication of the pozzolanicity of both PF and FA. As FA is an accepted SCM for the partial replacement of PC, PF having developed similar properties must also be recognised as a potential SCM for the partial replacement of PC. Given that the pozzolanic reaction has resulted in the consumption of the lime (and carbonated lime), SDT data also shows significant potential as a technique for the determination of the pozzolanic reactivity of potential SCMs.

CONCLUSION

From this experimental investigation, using SAI and SDT data, it may be concluded that PF demonstrates the attributes for classification as a pozzolan and for use as a SCM. Both PF and FA at low volume additions of 20% were found to conform to ASTM specifications, based on SAI measurements up to 91-days ageing. For both the low and high volume substitutions, PF and FA display comparable SAI values. Furthermore, PF and FA reveal an identical pattern of strength development with increasing age. The later stage SAI results, in particular, convey the benefits of using these pozzolans as SCMs for the partial replacement of PC in blended cements. The PF used had a coarser particle size distribution than the FA which resulted in lower SAIs for the PF blended cements. It is expected, however, that this difference would be corrected (i.e. similar SAI values would be attained) if the particle size distribution of the PF was reduced to that of the FA.

PF has been observed to perform in a comparable manner to FA, the industry standard SCM. The use of PF for the partial replacement of PC, therefore, has the potential to help minimise greenhouse gas emissions through the reduction in consumption of PC. As the PF is also a waste product produced during the quarrying and crushing of the pitchstone for lightweight expanded perlite applications, the use of this pozzolanic waste material as a SCM additionally helps mitigate the environmental impact at the mine site. Graded pitchstone fines incorporated as a SCM, therefore, show significant potential for reducing costs, curbing energy consumption and minimising environmental impact of the manufacture and application of cement-based building materials. From an engineering perspective, PF could also change and revolutionise the way PC is utilised in concrete, eventuating in value added benefits of long-term ultimate strength development.

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Table 1: Chemical analysis of raw materials by XRF method

Chemical Composition	PC (%)	PF (%)	FA (%)	A %
SiO_2	20.5	68.53	65.9	98.4
Al_2O_3	4.5	12.94	24.0	0.69
Fe_2O_3	4.5	1.04	2.87	0.11
CaO	64.9	0.9	1.59	0.02
MgO	1.2	0.02	0.42	0.02
Na_2O	0.0	4.51	0.49	0.03
K_2O	0.46	2.58	1.44	0.17
LOI		7.90	1.53	

Table 2: Particle size grading of waste PF and FA

Particle size (mm)	PF retained (%)	PF passing (%)	FA retained (%)	FA passing (%)
0.600	0.0	100.0	0.0	100.0
0.300	0.0	100.0	0.0	100.0
0.150	0.0	100.0	0.0	100.0
0.075	0.7	99.3	2.7	97.3
0.045	27.1	72.3	9.3	88.0
<0.045	72.3	0.0	88.0	0.0

Table 3: Mixture design proportions of mortar specimens

Mixture	PC (grams)	PF (grams)	FA (grams)	A (grams)	Water (grams)	HRWRA (mL)
$100PC_{wc}$	500.0	0.0	0.0	1375.0	241.6	0.6
$20PF_{wcm}$	400.0	100.0	0.0	1375.0	241.1	1.4
$20FA_{wcm}$	400.0	0.0	100.0	1375.0	241.9	0.2
$40PF_{wcm}$	300.0	200.0	0.0	1375.0	240.6	2.2
$40FA_{wcm}$	300.0	0.0	200.0	1375.0	241.9	0.2

Table 4: Strength Activity Index (SAI) of mortar mixtures

Mixture	7-day SAI (%)	28-day SAI (%)	91-day SAI (%)
$100PC_{wc}$	100	100	100
$20PF_{wcm}$	78	87	96
$20FA_{wcm}$	77	89	97
$40PF_{wcm}$	48	60	73
$40FA_{wcm}$	54	67	83

Figure 1: SAI (%) versus age (days) for 0%, 20% and 40% pozzolan substitutions (solid black line indicates = 75% pozzolan classification pass limit)

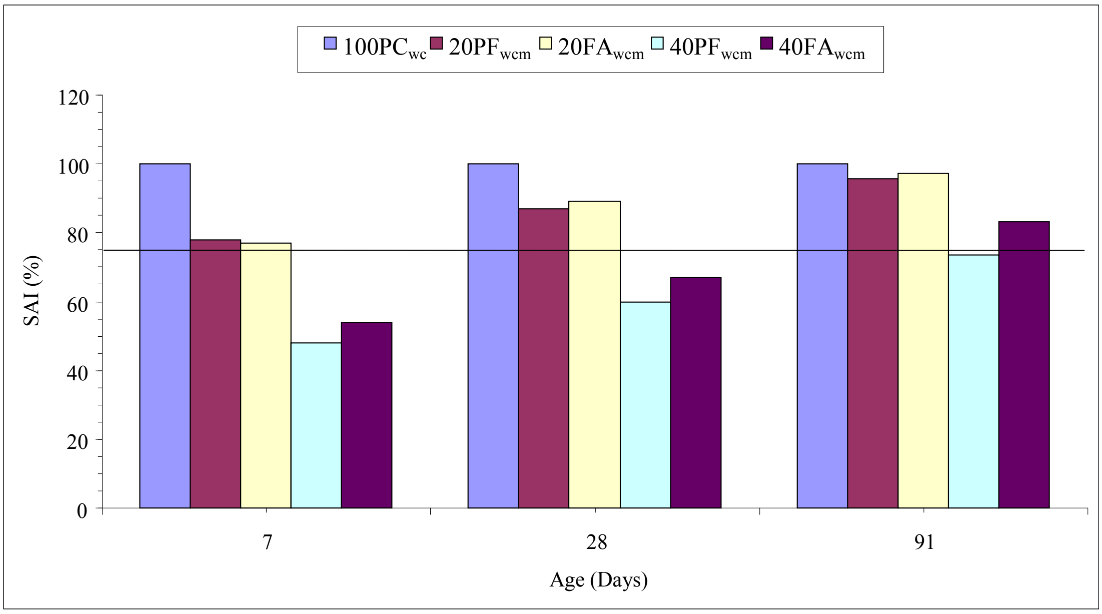

Figure 2: SDT thermograms for 0% and 40% pozzolan substitutions