

Pitchstone Fines Pozzolanic Activity Assessment As Partial Portland Cement (PC) Replacements

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ABSTRACT:

Mined pitchstone fines (PF), derived as a waste by-product from expandable perlite production in Australia, are a viable, environmentally friendly aluminosilicate supplementary cementitious material (SCM) suitable for partial Portland cement (PC) replacement, thus reducing greenhouse gas emissions resulting from PC manufacture. This paper reports on the findings of pozzolanic activity exhibited at 10%, 20% and 40% replacement levels of PC, through compressive strength determinations of mortar after 1, 7 and 28 days ageing, using strength activity index (SAI) criteria. Additionally, flows and wet densities have been examined using a polycarboxylic based high-range water-reducing admixture (HRWRA) superplasticiser and fixed water content relative to cementitious material present for all PF substitution levels.

KEYWORDS: Pitchstone, Perlite, Portland cement, pozzolan, supplementary cementitious material, strength activity index, flow, wet density

INTRODUCTION:

In the ceramics industry, new materials for use in engineering applications are categorised by their intended purpose as either traditional or non-traditional type ceramics. Traditional ceramics derived from common, naturally occurring raw materials, such as clays and quartz sand, comprise of the bulk of historical and present day manufactured building-construction industry products such as glass, bricks, mortar and concrete. Non-traditional ceramics, incorporating emerging "advanced" materials manufactured through specialised forming techniques, are representatives of highly refined materials exhibiting superior engineering properties. In the modern day, new materials featuring novel properties for use in ceramics based applications are evaluated on the two economic acceptance merits of commercial cost-effective manufacturing and reduced harmful greenhouse gas emissions.

Pitchstone is a glassy amorphous volcanic rhyolitic siliceous-aluminous acidic rock. Pitchstone is one of a group of materials that can be subdivided based on the internal hydrated mass content as obsidian (less than 2% water), perlite (between 2% to 5% water) or pitchstone (greater than 5% water) [1]. The well known perlite form can be expanded four to twenty times its size upon rapid heating depending on water content.

Depending on the intended building-construction application, pitchstone has the potential to be used as a raw material aggregate inclusion or as a supplementary cementitious material (SCM). Utilised as a SCM, pitchstone, as a prospective pozzolan, is defined as a silicate or aluminosilicate possessing little or no cementitious benefit, however, in a finely divided form and combined with water and calcium hydroxide, the principle component in PC, pitchstone will chemically react to form bonded compounds exhibiting cementitious properties [2].

For inert aggregate substitution, perlite within concrete and cementitious systems has been investigated in expanded form by Brouk [3, 4], Singh [5], Demirboga [6, 7] and Demir [8], due to its lightweight, thermal and acoustic insulative properties. The chemical properties revolving around the deleterious long-term durability effects of the alkali-silica reaction, expansion and main mechanical requirement of compressive strength have been investigated by Urhan and Demirboga [9-11]. In recent times, Turkmen [12] examined perlite expanded aggregates for use in self-compacting concrete (SCC), where workability and cohesiveness with high-range water-reducing admixture (HRWRA) superplasticisers in consolidation of low water-to-cement ratio (W/C) concrete, was examined in preventing segregation and bleeding of aggregates.

Table 2: Chemical analysis of raw materials by XRF method

Chemical Compositional	Sand (%)	PC (%)	PF (%)
SiO ₂	98.4	20.5	68.53
Al ₂ O ₃	0.69	4.5	12.94
Fe ₂ O ₃	0.11	4.5	1.04
CaO	0.02	64.9	0.9
MgO	0.02	1.2	0.02
Na ₂ O	0.03	0.0	4.51
K ₂ O	0.17	0.46	2.58

The use of perlite as a fine grained reactive pozzolan, either in the natural form of a mined ore or in its expanded state, has been reviewed by Bektas [13] in terms of its unique resistive ability to mitigate the alkali-silica reaction, thereby reducing the expansion of mortar and thus improving durability. In concrete, Yu [14] researched significant pozzolanic activity improvement for compressive strengths relative to a control equivalent at 91-days ageing, for 10% to 40% replacement of PC with perlite fines. In evaluating perlite fines with an equivalent particle size distribution to PC, Erdem et al [15] reported compressive strengths for 20% and 30% substitution levels, approaching control specimens at 91-days ageing. Preliminary investigations conducted by Ray et al [16] for 10% PC addition rates at 28-days ageing, also indicate that compressive strengths close to control are achievable, which in turn surpass the performance of equivalent fly ash pozzolanic replacement rates.

A large pitchstone (water content circa 7% to 8%) mining deposit in Australia, owned by Perlco Pty Ltd (PPL), located in the Nychum district near the town of Chillagoe in far north Queensland, provides vast resource of more than 100 million tonnes. This material is dehydrated, to produce expanded perlite grade related materials for use in construction, horticultural and industrial applications. The current primary crushing stage of the mined pitchstone ore, results in approximately 30% pitchstone fines (PF), all less than 500- μ m in size, from the initial pulverisation and final screening processes. As no current viable alternative use has yet been identified for the waste PF, stockpiles of the by-product material are stored on site [16].

This paper reports on the pozzolanic reactive classification of as received waste PF through ASTM C311-05 strength activity index determinations at 1-day, 7-day and 28-day ageing

Table 1: Particle size grading of waste PF

Particle Size (mm)	Retained (%)	Passing (%)
0.600	0.0	99.0
0.300	0.0	99.0
0.150	0.5	98.4
0.075	41.8	56.6
0.045	32.1	24.5
< 0.045	24.5	0.0

for 10%, 20% and 40% mortar PC replacements, using a fixed water-to-cementitious material ratio (W/CM) and superplasticiser for providing uniform workability [17].

METHODS AND PROCEDURES:

The following raw materials were used for all experimental mix mortar designs, having typical chemical compositions, as indicated by x-ray fluorescence (XRF) analysis (Table 1):

- Shrinkage limited Portland cement (Blue Circle Southern Cement Pty Ltd).
- Pitchstone fines (PF) (PPL).
- Raymond Terrace single washed sand (Rocla Quarry Products Pty Ltd).

Additionally, Glenium 51, a polycarboxylic-ether polymer based HRWRA, supplied by BASF Construction Chemicals Pty Ltd, was used as the source of superplasticiser.

Commercial construction grade fine aggregate sand meeting the exact grading requirements stipulated within ASTM C778-05 [18] was utilised, with the fine aggregate dried in ambient conditions to eliminate free water prior to use.

The particle size grading determination of PF was analysed by dry sieving against AS 1141.11-1996 criteria using washing prescribed in AS 1141.12-1996 over 45- μ m sieve inclusion size (Table 2) [19, 20].

Mortar cube specimens were prepared for 0% (PCW0), 10% (PCWCM10), 20% (PCWCM20) and 40% (PCWCM40) PF substitution amounts, all subjected to standard 1-day, 7-day and 28-day curing regimes, with the W/CM ratio fixed at 0.48 for PF substitutions.

Table 3: Mix design proportions of mortar specimens

Specimen	PC (grams)	PF (grams)	Sand (grams)	Water (grams)	Glenium 51 (mL)
PCWC0	500	- (0%)	1375	241.6	0.6
PCWCM10	450	50 (10%)	1375	241.2	1.2
PCWCM20	400	100 (20%)	1375	241.0	1.6
PCWCM40	300	200 (40%)	1375	240.3	2.6

Table 4: Flow (F), wet density (WD), compressive strength (CS) & strength activity index (SAI) data for 1-day (1D), 7-day (7D) & 28-day (28D) ageing date specimens

Specimen	F (%)	WD (kg/m ³)	1D CS (MPa)	7D CS (MPa)	28D CS (MPa)	1D SAI (%)	7D SAI (%)	28D SAI (%)
PCWC0	46	2141	14	28	36	100	100	100
PCWCM10	51	2150	12	26	32	86	93	89
PCWCM20	46	2123	10	22	30	71	79	83
PCWCM40	44	2093	5	14	20	36	50	56

Relative to ASTM C618-05 specified water requirement (WR) range, a fixed WR was employed for all PF substitution mixes, as an increase in W/CM was likely to decrease compressive strengths [21].

Mortar mix designs (Table 3) were taken from standardised proportions listed under ASTM C311-05, with the cementitious material-to-sand ratio (CM/S) fixed at 1:2.75 for all PF substitutions [17].

Preparation of mortar mixes were carried out in accordance with ASTM C305-99 and modified accordingly with an additional step in that prior to adding any PC to water, PF substitutions were allowed to mix with water for an additional 30 seconds on speed setting 140 ± 5 revolutions/min [22]. All superplasticiser additions were made directly to water before any commencement of mixing, following procedures stated in ASTM C1240-05, with the free water content in Glenium 51 superplasticiser taken to be 65% [23].

All flows were measured in accordance with the requirements listed under ASTM C1437-01 and wet densities were determined using a modified test method developed adhering to principles listed in ASTM C138/C138M-01a [24], using the rodding consolidation procedure [24, 25].

50-mm cube mortar specimens were cast in accordance with ASTM C109/C109M-05 specifications, using the hand tamping compaction

technique and meeting initial 24 hours moist environment curing criterion stipulated [26]. After 1-day ageing, compressive strengths were determined for 0%, 10%, 20% and 40% PF substitutions, with further 7-day and 28-day ageing results evaluated thereafter from appropriate curing immersion cycles in lime saturated water, prepared adhering to ASTM C511-05 specifications [27].

Compressive strengths on all cast 50-mm cube test specimens were determined using a calibrated Tinius Olsen Super L 600 kN hydraulic universal testing machine. Vernier callipers were used to measure the dimensions of the specimen cubes prior to compressive strength testing.

RESULTS AND DISCUSSION:

Flow:

A flow of approximately 50% was taken to be the reference point, as experimental mixes having higher flows beyond this value demonstrated bleeding and segregation. In early investigative trials, the control mix (PCWC0) was found to be less workable in the absence of HRWRA addition, making consolidation and hand compaction difficult for later wet density and compressive strength determinations. The flow tolerance permissible range for all PF substitution mixes compared to PCWC0 was taken to be $\pm 5\%$, as this is the norm stipulated by numerous standard test methods [17, 26].

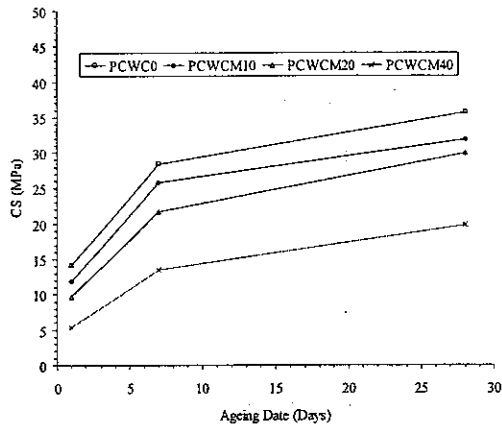


Fig 1: Compressive strengths (MPa) versus ageing date (days) for 0% (PCWC0), 10% (PCWCM10), 20% (PCWCM20) & 40% (PCWCM40) PF substitutions

For all PF substitutions, the degree of flow was found to comply with the acceptable tolerances (Table 4), as the superplasticiser volume significantly increased (Table 3). Increases of 200%, 267% and 433% HRWRA volume amounts were required for PCWCM10, PCWCM20 and PCWCM40 mixes, respectively, when compared to PCWC0. The increasing HRWRA additions suggest bleeding and segregation prevention is likely enhanced with increasing PF substitutions, for obtaining an equivalent degree of flow. This is not possible compared to using PC alone with these HRWRA increased volume additions, as both bleeding and segregation were observed to significantly increase for all these volume contents in preliminary trials.

Wet Density:

With increasing PF substitution, the corresponding wet densities were expected to decrease, as the specific gravity content of the PF substitution ($2,300 \text{ kg/m}^3$) was significantly lower than the specific gravity of the PC replacement ($3,150 \text{ kg/m}^3$). Apart from PCWCM10, the wet densities were seen to steadily decrease with increasing PF substitution, when compared to PCWC0 (Table 4). An increase of 0.4% was noted for PCWCM10, while decreases of 0.8% and 2.2% were observed for PCWCM20 and PCWCM40, respectively. The increase recorded for PCWCM10 can likely be explained by the corresponding flow value being 5% higher than PCWC0, suggesting that a higher degree of wetting was achieved with more cement particles dispersed, enhancing coating of finer PF particles, eliminating microscopic voids and providing improved packing of the structure. The wet densities decreasing with increasing PF substitutions likely suggest increasing PF content results in lighter-weight mortar.

Compressive Strength:

As expected, the compressive strengths with ageing, relative to initial 1-day results from 7-day to 28-day ageing periods were seen to markedly increase for increasing PF substitutions (Table 4 & Fig 1). For PCWC0, an increase from 200% to 257% after 7-day to 28-day ageing, respectively was noted, compared to the 1-day result, giving 57% enhancement in the 7-day to 28-day period. With PCWCM10, an increase from 217% to 267% was observed, giving a comparable 50% increase for this period. For PCWCM20, an increase of 220% to 300% was noted, showing an 80% increase during this ageing stage. With PCWCM40, a significant increase of 280% to 400% was seen, resulting in the largest increase of 120% for the 7-day to 28-day ageing period. There is a probable correlation between the magnitude of compressive strength differences significantly increasing relative to increasing PF substitution with ageing date, most apparent at 28-day ageing than at 7-day ageing.

Longer term ageing studies may possibly suggest further enhancements in compressive strengths with increasing PF substitution levels.

Strength Activity Index (SAI):

The strength activity index (SAI) is a measure of the pozzolanicity of a SCM and is measured as the strength relative to the control, in percent. For an SCM to be classified as a pozzolan, the SAI must be greater than 75% at 7-day and 28-day ageing (that is, the strength of the blended cement must not be less than 75% of the control strength) [21].

The SAIs of PCWCM10 and PCWCM20 (Table 4) after 7-day and 28-day ageing were found to meet the minimum permissible 75% limit, indicating appropriate pozzolanic reactive cementitious material classification. Even after 1-day ageing, PCWCM10 met the SAI requirement with an SAI of 86%, suggesting pozzolanic activity occurring in initial stages of strength development. For all the other PF blends, the SAI was found to increase with increasing ageing time suggesting a delay in strength development upon addition of the PF fines. The large increase in the 40% addition (PCWCM40) between 7-day and 28-day ageing suggests that even this blend could achieve the SAI requirement with further ageing. As the developing calcium-silicate-hydrate (C-S-H) gel is a phase responsible for strength development, it is likely that with increasing PF substitutions, formation of this phase is initially inhibited and then allowed to develop at a later stage, resulting in strength increasing with ageing.

CONCLUSIONS:

Pitchstone fines, as a potential pozzolan, have shown promise as a SCM when used as a partial PC replacement, while retaining the mandatory requirements of compressive strength. In this regard, PF additions of 10% and 20% were found to conform to ASTM standards based on the strength activity index measurements. A further benefit of the PF blends was that PF additions were found to reduce segregation and bleeding, thus aiding workability of the PC blends.

The use of PF for the partial replacement of PC has the potential to help minimise PC consumption and, hence, minimise the overall impact of harmful greenhouse gas emissions created during the manufacture of PC. The PF are also, currently, a waste material of an industrial process and, as such, the use of this material as a SCM also helps to mitigate the environmental impact at the mine site. Perlite fines, therefore, used as a SCM, show significant potential for the reduction of costs and energy consumption and the minimisation of environmental impact in the manufacture and application of construction materials.

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