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High strength blended cement concrete incorporating volcanic ash: Performance at high temperatures

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Abstract

The strength and durability of high strength blended cement concretes incorporating up to 20% of volcanic ash (VA) subjected to high temperatures up to 800 °C are described. The strength was assessed by unstressed residual compressive strength, while durability was investigated by rapid chloride permeability (RCP), mercury intrusion porosimetry (MIP), differential scanning calorimetry (DSC), crack pattern observations and microhardness testing. High strength volcanic ash concrete (HSVAC) exhibited better performance showing higher residual strength, chloride resistance and resistance against deterioration at high temperatures compared to the control high strength OPC concrete. However, deterioration of both strength and durability of HSVACs increased with the increase of temperature up to 800 °C due to weakened interfacial transition zone (ITZ) between hardened cement paste (hcp) and aggregate and concurrent coarsening of the hcp pore structure. The serviceability assessment of HSVACs after a fire should therefore, be based on both strength and durability considerations.

Keywords: High temperature; Volcanic ash concrete; Residual compressive strength; Chloride permeability; Microstructure

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1. Introduction

Research has been carried out on the use of volcanic ash (VA), volcanic pumice (VP), fly ash (FA), blast furnace slag (BFS), silica fume (SF), etc. as cement replacement materials [1–7]. The VA, VP, and FA are pozzolanic materials, because of their reaction with calcium hydroxide produced during the hydration of cement. Amorphous silica present in the pozzolanic materials combines with calcium hydroxide and forms cementitious materials. These materials typically improve the durability of concrete and can also reduce the rate of heat liberated due to hydration, which is beneficial for mass concrete applications.

Pozzolanic high strength concretes (HSC) are used extensively throughout the world; the oil, gas, nuclear, and power industries are among the major users. The applications of such concretes are increasing day by day due to their superior structural performance, environmental friendliness, and energy conserving implications [8]. Apart from the usual risk of fire, these concretes are exposed to high temperatures and pressures for considerable periods of time in the above-mentioned industries. Although concrete is generally believed to be an excellent fireproofing material, many recent studies have shown extensive damage or even catastrophic failure at high temperatures [9]. During the last decade, there has been extensive research on the fire performance of normal-strength concrete (NSC) as well as high strength concrete (HSC) incorporating FA, BFS and SF at elevated temperatures [10].

An earlier research on a 170-MPa HSC containing 14–20% SF indicated that silica fume concrete (SFC) is highly prone to spalling and cracking at elevated temperatures [11]. Five of the 15 100 × 200-mm cylinders of SFC exploded when heated to 650 °C and the residual compressive strength increased up to 350 °C and then decreased sharply. SFC with granite aggregate and SF contents of 0–10% (by weight of cement), did not explode when heated

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at rates of 1 °C/min and 5 °C/min to 600 °C [12]. It was concluded that SFCs at high moisture contents were more likely to explode and an upper limit of 10% on SF was suggested to avoid spalling. Sanjayan and Stocks [13] also came to the same conclusions after conducting a fire test on a monolithic beam-slab (T-beam) specimen containing 8% SF. Sarshar and Khoury [14] found that the residual strengths of the SFCs with 10% SF at elevated temperatures were worser than the 100% ordinary Portland cement (OPC) concretes. Hammer [15] tested SFCs containing 0–5% SF and normal-weight crushed gravel or lightweight aggregates subjected to a maximum temperature of 600 °C at a heating rate of 2 °C/min. Concrete without SF showed slightly better performance in terms of lower strength loss and reduced spalling. Felicetti and Gambarova [16] also obtained the similar results. In summary, it can be concluded that the addition of SF highly densifies the pore structure of concrete, which can result in explosive spalling due to the buildup of pore pressure by water vapors. Since the evaporation of physically absorbed water starts at 80 °C, which induces thermal cracks, such concretes show inferior performance in terms of strength and durability as compared to OPC concretes at elevated temperatures.

The research on performance of pulverized fuel ash (PFA) concretes at elevated temperatures dates back to 1969 [17]. Nasser and Marzouk [18] conducted a series of research on 25-MPa mass concrete containing 25% lignite fly ash by weight exposed to high temperatures of 21–232 °C for periods of over 6 months. The strength of the PFA concretes was found to increase in the temperature range of 121–149 °C that was as high as 152% of the original strength. However, the strength was reduced to about 27% of the original value when the exposure temperature was raised to 232 °C. It was suggested that the increase in strength for the PFA concretes was due to the formation of tobermorite (a product of lime and PFA at high pressure and temperature), which was reported to be two to three times stronger than the CSH gel. A similar increase in strength between 200 °C and 250 °C in a 90-MPa HSC incorporating Class F FA was reported [19].

Ghosh and Nasser [20] conducted research to investigate the effects of temperature (21–232 °C) and pressure (5.2–13.8 MPa) on the strength and elasticity of HSC incorporating SF (10% by weight) and high-calcium lignite FA (20% or 60%) together. A gradual deterioration of strength and static modulus of elasticity was observed with a rise in temperature at all pressures. The 20% PFA replacement showed more loss; however, in any case, the residual compressive strength was more than 60% of the original strength.

Wong et al. [21] studied the effects of PFA replacement level, water/binder ratio (W/B), and curing conditions on the residual properties of concrete at elevated temperatures. An increase in strength was observed at 250 °C. All PFA concrete specimens showed better performance up to 650 °C than pure OPC concrete specimens; however, after that, there was no significant difference in the residual strength of all specimens. It was found that a high dosage of PFA enhanced the residual properties of concrete at elevated temperatures. Conclusively, it was found that the PFA improved the performance of concrete at elevated temperatures as compared to SF or OPC concretes. However, this improvement was more significant at temperatures below 600 °C. PFA also reduced the surface cracking of concrete both at elevated temperatures and after post-cooling in air or water [22].

Diederichs et al. [19] prepared three HSCs mixes incorporating condensed silica fume (CSF), PFA, and granulated BFS independently. The mixes were subjected to a maximum temperature of 900 °C. The BFS concrete showed the best performance followed by PFA and SF concretes.

Sarshar and Khoury [14] prepared cement paste and concrete specimens incorporating 65% BFS by weight of cement and firebrick aggregates. The results were compared with OPC cement paste/concrete and 30% PFA cement paste. The maximum temperature was 700 °C, while the residual properties were measured at every 100 °C interval. The BFS–OPC paste and concrete gave the best results among all the specimens tested. The residual compressive strengths of BFS concrete were 102% and 80% of the initial cold strength at 450 °C and 600 °C. Additionally, Sullivan and Sharshar [23] studied the properties of SF and BFS concretes prepared with two thermally stable aggregates (viz., Lytag and crushed firebrick). The results indicated that concretes with the lightweight aggregate (i.e., Lytag) had lower residual strength at temperature above 150 °C than the corresponding concrete prepared with firebrick aggregate. The use of firebrick with BFS in concrete also resulted in superior elevated temperature performance. Poon et al. [24] compared the strength and durability performance of different pozzolanic HSCs incorporating CSF, PFA, and ground BFS, at elevated temperatures subjected to heating levels of 200 °C, 400 °C, 600 °C, and 800 °C.

Volcanic materials such as VA and VP are found abundantly in volcanic areas around the world. Finding new and improved ways to build with such materials is becoming widespread. Comprehensive research has been conducted over the last few years on the use of VA and VP in cement and concrete production [1,2,25–27]. Research suggested the manufacture of blended cements replacing up to 20% OPC by VA and VP [1].

Durability of concrete is one of its most important desirable properties and it is essential that the concrete made with VA and VP blended cement should be capable of preserving its durability throughout the life of structures like other pozzolanic concretes made with SF, FA, PFA and BFS [25–27]. No research has been conducted especially on the performance of VA based high strength pozzolanic concrete at elevated temperature. This paper presents the results of a comprehensive experimental investigation studying (at macro- and micro-levels) the strength and durability characteristics of high strength volcanic ash concrete (HSVAC) subjected to elevated temperature.

2. Experimental program

2.1. Materials

The VA used in this investigation was collected from the Rabaul area of the East New Britain Province of PNG and the source was a volcano called Mount Tavurvur. The Rabaul area is situated in the worldwide earthquake and volcanic zone known as the 'Belt of fire'. The cement used was locally manufactured OPC conforming to ASTM Type I. Ordinary drinking water was used in all concrete mixes.

Chemical and physical properties of VA and OPC used in this investigation are presented in Table 1. VA is principally composed of silica (about 60%) while the main component of OPC is calcium oxide (maximum 70%). VA also has compounds like calcium oxide, alumina and iron oxide (total about 31%). The Blaine fineness and oven dry bulk density of VA are 285 m^2/kg and 2450 kg/m^3, respectively. VA satisfies the requirement of Class F fly ash as per ASTM C 618-91. The OPC has a specific gravity of 3.15 and Blaine fineness of 320 m^2/g.

Table 1
Chemical and physical properties of cementing materials

Chemical compounds	Volcanic ash (%)	OPC (Type I) (%)
Calcium oxide (CaO)	6.1	64.1
Silica (SiO_2)	59.3	21.4
Alumina (Al_2O_3)	17.5	5.7
Iron oxide (Fe_2O_3)	7.0	3.5
Sulphur trioxide (SO_3)	0.7	2.1
Magnesia (MgO)	2.6	2.1
Sodium oxide (Na_2O)	3.8	0.5
Loss on ignition	1.0	1.1
Fineness, m^2/kg	285	320

Table 2
Grain size distribution and properties of materials

Grain size distribution of aggregates			Physical properties aggregates and VA			Water absorption (%)
Sieve size (mm)	Fine % passing	Coarse % passing		Bulk density (kg/m^3)		
				Oven dry	SSD	
20	100	100	Coarse	2570	2640	2.49
12.7	100	71	Fine	2610	2660	0.60
9.5	100	28				
4.75	93	0				
2.36	70.5		VA	2450	2440	0.41
1.18	51.5					
0.6	35					
0.3	20.5					
0.15	8.5					

The fine and coarse aggregates were local natural river sand and crushed limestone with maximum nominal sizes of 20 mm. The particle size distributions as per ASTM C 136-01 for aggregates and VA are presented in Table 2. The bulk density and water absorption of aggregates and VA are also presented in Table 2. A naphthalene–formaldehyde condensate was used as a superplasticizer (SP) in HSVAC mixes. This SP was a brown liquid containing 41.2% solids.

2.2. Mix proportions and mix details

The mix proportions of high strength volcanic ash concrete (HSVAC) mixes are shown in Table 3. VA was introduced as a cement replacement (0–20% by mass) material. Concrete mix proportions were decided from the experience of previous research to achieve optimum strength and durability [2,25,26,28]. HSVACs were designed based on an OPC control mix having a 28-day compressive strength of about 80 MPa. All mixtures were produced at a slump of over 80-mm (as per ASTM C 143-00) with a constant water-to-binder ratio (W/B) of 0.30. Air entraining admixture was not used. SP dosages were based on solid content (Table 3). The air contents of mixtures were determined by pressure meter as per ASTM C 231-97. The 28-day compressive strength and air content of concrete mixtures are presented in Table 3. The air content ranged between 2.6% and 3.2%. One-hundred mm concrete cubes and 100 (diameter) × 200-mm concrete cylinders were cast.

2.3. Curing conditions

The specimens were demoulded 24 h after the casting and placed in a water tank at 25 °C. After 28 days of water curing, they were transferred to an environmental chamber maintained at 25 °C and 75% relative humidity. The specimens were kept there for 4 weeks until heating.

Table 3
Mix proportion of high strength volcanic ash concrete (HSVAC) mixtures

Mix ID	VA (%)	W/B	Water (kg/m^3)	Cement (kg/m^3)	Aggregates		SP[a](%)	Air content (%)	28-day compressive strength (MPa)
					Fine (kg/m^3)	Coarse (kg/m^3)			
VA-0[b]	0	0.30	150	500	760	1016	0.50	2.6	79.5
VA-5	5	0.30	150	475	754	1016	0.95	2.8	82.4
VA-10	10	0.30	150	450	748	1016	0.95	3.0	75.3
VA-15	15	0.30	150	425	742	1016	0.85	3.1	67.4
VA-20	20	0.30	150	400	736	1016	0.80	3.2	61.5

[a] SP content (based on solid mass) in percentage by weight of binder Numerics in mix designation represent percentage of VA.

[b] Control HS OPC concrete.

2.4. Heating and cooling regimes

At an age of 56 days, the specimens were heated in an electric furnace up to 200, 400, 600, and 800 °C. Each temperature was maintained for 1 h to achieve the thermal steady state [29]. The heating rate was set at 2.5 °C/min as used in previous research studies with a view to have a comparative performance study [30]. However, the rate of heating is significantly lower than the standard fire rate of temperature rise specified by ASTM E 119a-00, which is about 600 °C in the first 6.7 min. The specimens were then allowed to cool naturally to room temperature.

2.5. Specimen dimensions and testing details

Compressive strength test was performed on 100-mm concrete cubes according to BS 1881: Part 120:1983. Three specimens were tested at each stage and average values are reported. There are three approaches for testing concrete in compression within a high-temperature context: stressed tests, unstressed tests, and unstressed residual tests [9]. The first two types of test are generally used for assessing the strength of concrete at high temperature, while the last is generally used for finding the residual properties, after cooling down to room temperature. With regard to the unstressed residual tests, one should note that the strength measured in this way is the smallest, since the lack of transient creep and partial rehydration of the cement during and after cooling induce further damage in the concrete mass [9].

Immediately after cooling of the heated concrete cubes, the crack widths were measured using a digital microscope that can measure the surface crack widths up to 1 μm. For the examination of internal crack patterns, the conventional method of cutting the specimens into slices would not be appropriate as this would create more cracks in these fired damaged weaken concrete during the cutting process. To overcome this problem, each concrete cube specimen was precut into three slices, and the slices were assembled back to the original cubical form when they were subjected to heating.

Rapid chloride permeability (RCP) test was conducted as per ASTM 1202-97 on 100 × 50-mm concrete slices (prepared from concrete cylinders) to determine permeability and resistance to chloride ion penetration. The chloride ion resistance of concrete gives an indirect measure of its permeability and internal pore structure, as more current passes through a more permeable concrete.

The porosity and pore size distribution were measured using Mercury Intrusion Porosimetry (MIP), which had a measuring pressure ranging from 0.01 to 200 MPa [27]. The contact angle selected was 140° and the measurable pore size ranged from 0.004 to 144 μm. The Washburn equation was used to calculate the pore radii [31]. The samples in the form of pellets of about 5 mm in size, consisted of hardened cement mortar, were collected from the crushed concrete cubes and immediately soaked in acetone to stop the further hydration. The samples were dried in an oven at 60 °C for 48 h before testing.

The differential scanning calorimetry (DSC) test was performed on the hardened mortar samples taken from the crushed concrete cubes (at 25 °C) after 56 days of curing to determine the quantity of $Ca(OH)_2$ formed in mortars. The samples used weighted around 60 mg. The samples were heated at a constant heating rate of 10 °C per minute to 1100–1200 °C, in a dynamic helium atmosphere. The DSC data analysis gave graphs of heat flow between the sample and reference crucibles versus temperature. DSC thermograms showed peaks due to endothermic (heat absorbing) and exothermic (heat releasing) reactions. The $Ca(OH)_2$ content was equivalent to the area (enthalpy) under the respective endothermic peaks. The size of the area under the curve was related to the quantity of the material in the sample.

Based on the ASTM E384-99 testing method, a Vickers indenter was used to determine the microhardness in bulk pastes and in the transition zone between aggregates and hardened cement paste (hcp). To eliminate the influence of dispersed sands on the transition zone, mixes without fine aggregates were also cast into cylinders. Slices cut from the middle of the cylinders were polished with 600# paper then 1500# paper to obtain an adequate surface with a minimum of damage. Slices were then carefully sealed to avoid carbonation, which might lead to larger measured hardness values because the carbonation product ($CaCO_3$) is much harder than the reactants. As the typical width of the interfacial transition zone (ITZ) is about 50 μm, the applied load in the microhardness test was determined to be 0.05 N so that the spacing between indentation points should be at least two times the diagonal of the indentation while ensuring a sufficient number of points was taken to map the ITZ [32]. The measured range was up to 100 μm away from the surface of aggregates although the actual width of the transition zone can be far smaller than 50 μm. The profiles of microhardness were derived based on average values of six determinations at each indentation point. Beyond 400 °C, cracking along the boundary between aggregate and hcp was inevitably obvious, making it impossible to obtain accurate data on the ITZ. Therefore, the reported microhardness values in the ITZ in this research are results on unheated concretes and concretes exposed only to 200 °C. Microhardness test data on bulk pastes in unheated concretes and in concretes exposed to 200, 400, 600 and 800 °C are also reported.

3. Test results and discussion

3.1. Residual compressive strength

The residual compressive strength test results are shown in Fig. 1. The test results indicated that each temperature range had a distinct pattern of strength loss or gain.

From 25 °C to 200 °C, HSVACs showed an increase in strength (Fig. 1) with the highest increase in strength of

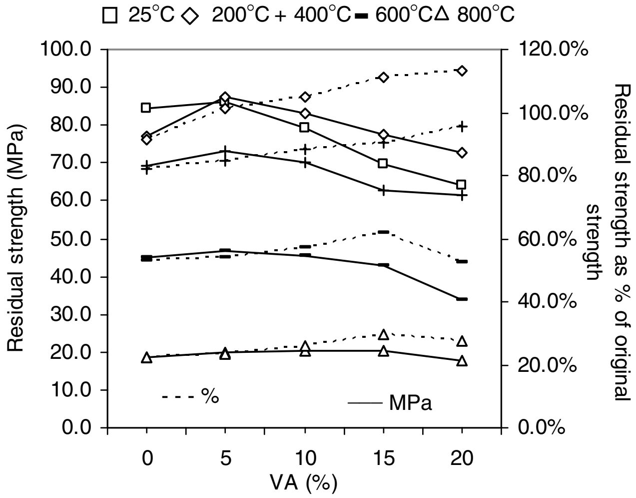


Fig. 1. Variation of residual compressive strength with VA content and temperature.

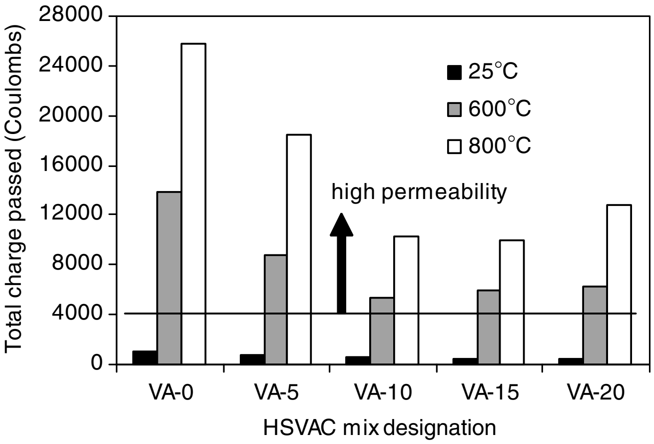


Fig. 2. Effect of high temperatures on the chloride ion resistance of HSVACs.

about 14% in 20% VA concrete. The strength gain was probably due to the formation of tobermorite from the reaction between unhydrated VA particles and lime at high temperatures [18]. However, no test was conducted in this study, to confirm the formation of tobermorite. The strength of the control HS OPC concrete was decreased by about 9% (Fig. 1). No visible cracking or spalling was observed in this temperature range.

From 200 °C to 400 °C, a decrease was observed in HSVACs, which was 4–15% of the original strength (Fig. 1). Again, pozzolanic HSVACs performed better and showed higher residual strength compared with control HS OPC concrete (Fig. 1).

A severe loss in strength was observed in the 400–600 °C temperature range. The strength loss was within the range of 38–48% (Fig. 1). HSVACs performed better and showed no spalling or cracking except hairline cracks. At 800 °C, all concretes showed severe deterioration possibly due to the decomposition of CSH gel [33]. The residual strength at this temperature ranged between 23% and 29% (Fig. 1).

Generally the strength loss decreased with the increase of VA content when the temperature was varied from 200 to 800 °C. This was an indication of better performance of HSVACs in retaining the strength at elevated temperature as compared to control OPC concrete. The deterioration of strength at elevated temperature for such concretes can be attributed to the coarsening of the pore structure and increase in pore diameter [30]. The beneficial effect of VA was more pronounced at temperatures below 600 °C. Spalling was observed in 8% of the control HS OPC concrete specimens, while HSVACs only showed visible network of fine surface cracks.

3.2. Resistance against chloride ion penetration

The influence of VA content and elevated temperature on the RCP of HSVACs is shown in Fig. 2. It is important to note that this test was performed only on specimens subjected to 25 °C, 600 °C and 800 °C as more damage occurred at those temperatures. Long testing time was another reason to limit the extent of this analysis. Only those specimens that did not show very extensive cracking were selected, as this test is insensitive to cracked specimens.

A close examination of these results indicated a clear relationship between the residual compressive strength and concrete permeability, as more permeable specimens showed more pronounced loss of compressive strength (Fig. 3). All HSVACs showed very low permeability before subjected to elevated temperature. As the temperature was increased, a severe loss in impermeability was observed. In percentage of original value, this loss was as much 3000% and far more than the loss in compressive strength (Fig. 2). The ASTM C 1202-97 specifies the concrete as highly permeable if the charge that passes through it is more than 4000 C. Since all specimens showed values higher than 4000 C after fire, such concretes can be considered as non-durable depending upon the situation, even if

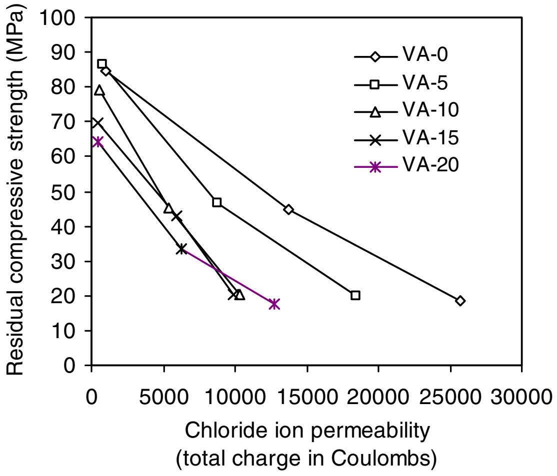


Fig. 3. Relation between residual compressive strength and permeability.

they retain a higher proportion of their compressive strength. A comparison among different concretes showed better chloride resistance and lower permeability of HSVACs as compared to control HS OPC concrete even at elevated temperatures.

3.3. Porosity and pore size distribution measurements

The porosity and pore size distribution were measured using MIP for specimens subjected to temperatures of 600 °C and 800 °C. It should be noted that there are uncertainties related to pore size distribution measured by MIP especially due to the presence of cracks [34]. The MIP test results clearly indicated an increase in porosity and average pore diameter with the increase in temperature (Figs. 4 and 5). This effect can be related to the coarsening of the pore structure [30,35] and was responsible for the strength and impermeability loss. A significant decrease in porosity and average pore diameter was observed in HSVACs by the addition of VA as compared to the control HS OPC concretes even at elevated temperatures. Fig. 6 compares the pore size distributions of control HS OPC concrete (VA-0) with those of HSVACs (VA-20) at 25 °C and after exposure to 800 °C. The cumulative volume of pores larger than 0.01 μm, which influences the concrete strength was greatly increased after subjected to high temperature [30]. The beneficial effect of the addition of VA can be identified from the lower volume of pores (larger than 0.01 μm) in VA concretes compared to OPC concretes before and after exposure to high temperature (Fig. 6).

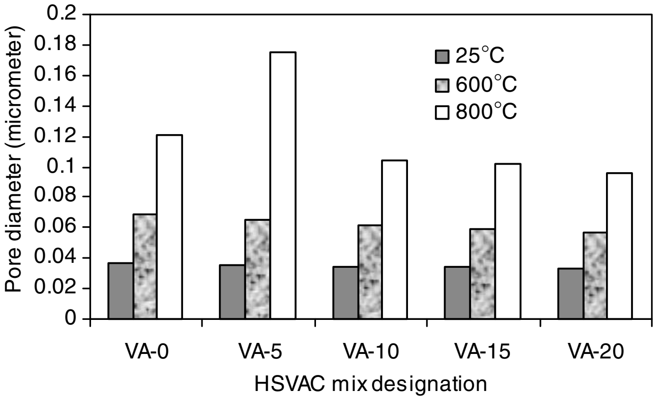


Fig. 4. Effect of temperature and VA content on the pore size.

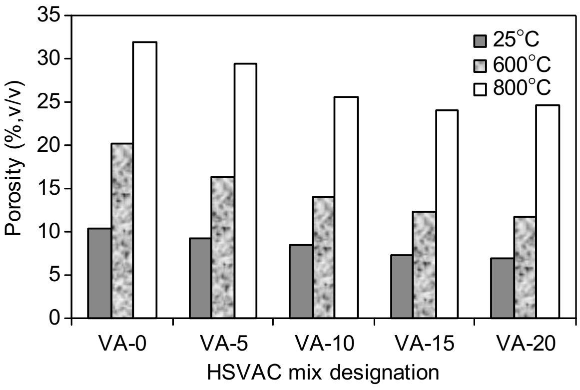


Fig. 5. Porosity of HSVACs as a function of temperature and VA content.

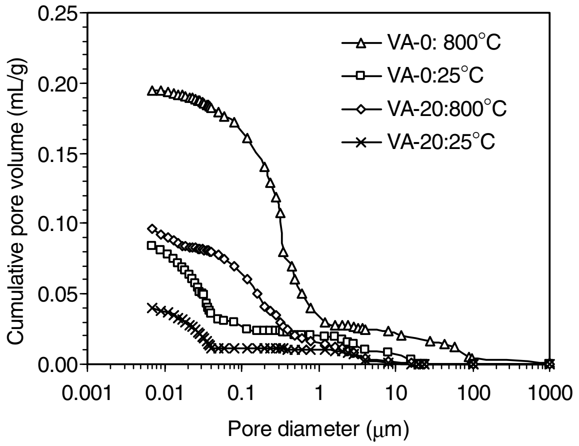


Fig. 6. Pore size distribution before and after exposure to high temperature.

3.4. Analysis of compressive strength and durability

To compare the performance of different HSVACs integratively, two deterioration indices, d_{ms} and d_{pd}, as defined by Chan et al. were used [30]. The index d_{ms} is the deterioration index of mechanical strength and d_{pd} is the deterioration index of the permeability-related durability. These indices can be defined by Eqs. (1) and (2).

$$d_{ms} = 1 - \frac{f_{rc}}{f_c} \tag{1}$$

$$d_{pd} = 1 - \frac{\sum V_p}{\sum V_{pf}} \tag{2}$$

where f_{rc} = mean residual compressive strength after fire; f_c = mean original compressive strength before fire; $\sum V_p$ = cumulative volume of pores larger than 1.3 μm before fire and $\sum V_{pf}$ = cumulative volume of pores larger than 1.3 μm after fire.

The indices can have values ranging from 0 (no deterioration) to 1 (full deterioration). The calculated values of d_{ms} and d_{pd} are given in Table 4. The deterioration indices (d_{ms} and d_{pd}) increased with the increase of temperature

Table 4
Values of deterioration indices d_{ms} and d_{pd}

Mix ID	d_{ms}				d_{pd}	
	200 °C	400 °C	600 °C	800 °C	600 °C	800 °C
VA-0	0.088	0.181	0.469	0.779	0.681	0.911
VA-5	−0.014	0.154	0.459	0.768	0.672	0.874
VA-10	−0.049	0.116	0.429	0.742	0.665	0.822
VA-15	−0.113	0.098	0.384	0.706	0.597	0.828
VA-20	−0.135	0.043	0.476	0.724	0.644	0.840

from 200 to 600 °C and generally decreased with the increase of VA content from 0% to 20% (Table 4). At 200 °C, the increase in VA actually found to be beneficial in increasing the resistance against the compressive strength deterioration as indicated by the negative values of d_{ms}. The control OPC concrete deteriorated more compared to the HSVACs with respect to both mechanical strength and permeability characteristics. This can be related to the significant decrease in porosity and average pore diameter by the addition of pozzolanic VA in HSVACs as described earlier.

The deterioration indices also indicated a severe loss of durability as compared to the compressive strength, and indicated that even after the fire, if concrete retained a high proportion of its original compressive strength, an examination of durability should be made. This is important as the loss in durability can result in deterioration of concrete and rusting of rebars, which may reduce the overall life of the structure.

3.5. Crack width and pattern analysis

The surface cracks started to appear at around 300 °C and continued to grow till the final rise in temperature up to 800 °C. The crack widths are reported in Table 5. Fig. 7 shows typical crack patterns observed in different concretes at 800 °C.

The crack widths decreased with the increase of VA content and at the same time increased with the increase of temperature. The control OPC concrete specimens showed one or two major cracks usually in the middle of the specimen, but no splitting occurred even at 800 °C. HSVACs showed a network of minor cracks, but no major crack was observed that would cause disintegration.

Table 5
Surface crack widths in concrete specimens and DSC test results

Mix ID	Crack widths (mm)				$Ca(OH)_2$ (J/g)
	600 °C		800 °C		
	Min	Max	Min	Max	Endothermic peak area
VA-0	0.35	1.38	0.82	2.02	105
VA-5	0.24	1.21	0.69	1.71	83
VA-10	0.17	1.08	0.54	1.46	72
VA-15	0.21	1.2	0.57	1.58	54
VA-20	0.23	1.27	0.58	1.64	39

As far as the crack widths after fire are concerned, they were well above the maximum crack widths specified by the ACI (0.10 mm for wet conditions and 0.41 mm for dry conditions) [24]. It was also observed that although the surface cracking started at around 300 °C, the internal cracks commenced after 600 °C. As the temperature of the internal concrete during a short heating period is usually lower than the surface temperature, the internal concrete can be considered as durable. This was particularly advantageous for HSVACs, which showed a network of fine cracks that can be refilled by post fire curing [36].

3.6. Microhardness

Fig. 8 shows variation of ITZ ranges, i.e., where the microhardness test resulted in lower Vickers hardness numbers (Hv) than those in the middle of the hardened bulk cement pastes, after concretes were exposed to 200 °C. For concretes made with OPC only, the extent of the weak

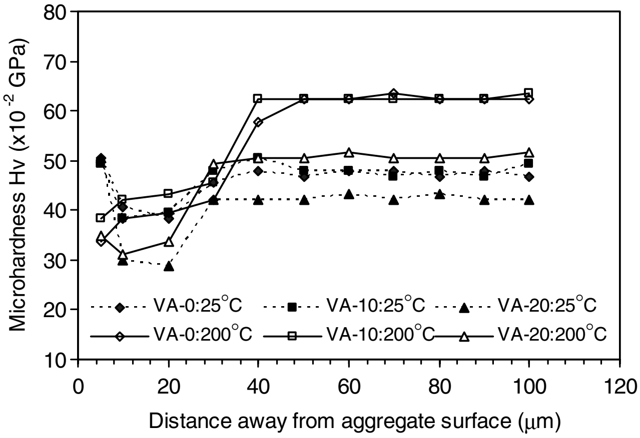
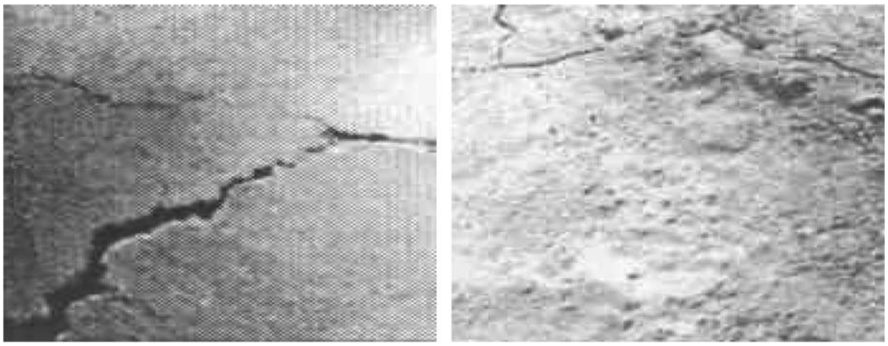


Fig. 8. Influence of VA and temperature on microhardness profiles in the ITZ.



HS OPC (VA-0): Control HSVAC (VA-20)

Fig. 7. Crack patterns at 800 °C.

zones (ITZ range) increased from about 35 μm (at 25 °C) to about 50 μm (at 200 °C). For concrete made with 10% VA, the weak zone was extended from about 35 μm (at 25 °C) to about 40 μm (at 200 °C). The presence of VA resulted in a beneficial effect when VA was added to replace 20% of OPC by weight—no obvious increase in width of the weak zone (ITZ range) was observed.

Increased microhardness values in the vicinity of the aggregate were observed in all unheated specimens, and these may be due to the presence of stiff inclusions in the excited range around the indentation, which restrains the flow of material under the indentation [32]. After exposed to 200 °C, further decreased Hv values in the vicinity of aggregates were observed in all concretes. This typical deterioration in ITZ may indicate the separation of hcp from the aggregate. In addition, improvement of microhardness within the ITZ was observed in concrete made with VA but it was clear in HSVACs with 20% VA, which may be attributed to the superior fire resistance of VA concretes.

Microhardness test results on bulk pastes exposed to high temperatures are shown in Fig. 9. The trends of microhardness versus percent of VA curves were quite similar to those of the compressive strength versus percent of VA curves shown in Fig. 1. However, the percentage rises in Hv values at 200 °C (ranged between 110% and 126%) were even higher than the percentage improvements in compressive strengths (ranged between 101% and 114%). When the exposure temperatures were raised to 400 °C, the Hv values for pastes with 0% and 10% VA were about 7% lower while Hv values for pastes with 20% VA were about 8% higher compared to the results on unheated specimens (25 °C). Microhardness dropped significantly when the exposure temperature was as high as or more than 600 °C (Fig. 8). This can be attributed to the decomposition of CSH and $Ca(OH)_2$ beyond 600 °C causing hydrates to lose their binding properties [37].

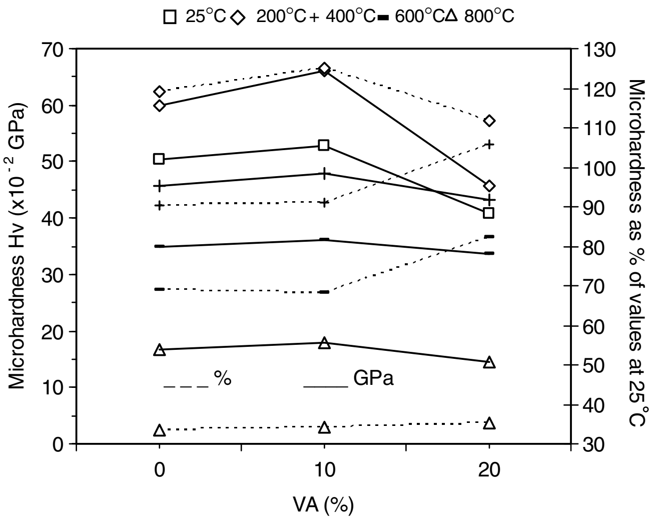


Fig. 9. Influence of VA content and temperature on the microhardness of hcp.

3.7. DSC test results

Table 5 shows the results of DSC at a curing age of 56-day. The quantity of $Ca(OH)_2$ formed in the hydration of the mortar decreased with the addition of VA and much of the reduction in $Ca(OH)_2$ content is related to the higher substitution of VA for cement. The endothermic peak for $Ca(OH)_2$ was observed at around 450 °C. Lowering of $Ca(OH)_2$ also indicated that the pozzolanic reactivity of VA consumes $Ca(OH)_2$ resulting from the hydration of cement. The pozzolanic reaction of VA with $Ca(OH)_2$, should improve the corrosion resistance of HSVACs compared to control OPC concrete [28]. This was justified from the higher chloride resistance of HSVACs compared to control concrete as observed in the current study. VA was added as fine granulates and upon hydration it had the capability of partially obstructing voids and pores. This lead to a decrease of pore size with refinement of pore structure and to a smaller effective diffusivity for chloride or other species as confirmed from the experimental results (Figs. 2–4). This can improve the long-term corrosion resistance of VAC based structures. Similar phenomena were also observed in FA concrete and VA based mortar [26,38].

4. Fire resistance mechanism of HSVAC

When concretes are exposed to high temperatures, there are changes in the mechanical properties and the durability of concrete. However, the mechanisms causing the changes in properties are quite complex as a result of the concurrence of chemical and physical changes in hcp, aggregate, and at the interfaces.

After concretes were exposed to a temperature of 200 °C, an increase in compressive strength was observed in HSVACs with 10–20% VA, with an even more pronounced increase of microhardness in the bulk hcp, but the durability of concretes was degraded. The increase of compressive strength can be partially due to the strengthened hcp during the evaporation of free water, which leads to greater Van der Waal's forces as a result of the cement gel layers moving closer to each other [22,39]. Because transportation of moisture in concrete is rather gradual, residual moisture in concrete allowed accelerated hydration at the early stage of heating concretes to high temperatures. Further hydration of cementitious materials is another important cause of the hardening of hcp. Especially for VACs, unhydrated VA particles can react with calcium hydroxide and produce CSH like gels [39]. The hardening effect is compatible with the microhardness tests results on the bulk pastes. However, weakening of the ITZ between aggregate and hcp also occurred during the exposure to 200 °C. At the same time, the microhardness profiles in the ITZ showed further decrease of Hv around aggregates, indicating that tiny cracks may have initiated along the boundary. At such an exposure temperature, coarsening of the pore structure of cement paste also occurred. Fortunately, the hardening effect can compensate for the loss of strength caused by the coarsening of the cement paste and the weakening of the ITZ. With respect to the durability of concrete exposed to 200 °C, the weakened transition zone played the predominant role in the nearly doubled values observed in the rapid chloride permeability test. Since microcracks might have developed along the boundary due to the swelling of physically bound water layers and thermal incompatibility between aggregates and cement pastes [40], the path for ion penetration was shortened [41]. In addition, increased porosity in the hcp also made penetration of chloride easier.

During exposure to 400 °C, coarsening of hcp occurred with a concurrent drop in hardness. Dehydration became the predominant influence although thermal hydration played a more effective role in case of heating to 200 °C [39]. Microcracking also increased significantly beyond 300 °C, which is responsible for the further degradation of durability for specimens heated to 400, 600 and 800 °C [42]. The gain of strength after heating to 200 °C was lost after concretes were heated to 400 °C. The loss of compressive strength was in good agreement with the decrease in microhardness in bulk pastes when exposure temperatures were raised from 200 °C to 400 °C. Decomposition of the major hydrate, known as CSH, was inevitable as the exposure temperature was raised to 600 °C [37], causing severe coarsening in its microstructure of pastes and the loss of binder property. Hence sharp drops in microhardness values and compressive strengths were observed together with a significant increase of chloride diffusion in concretes. Disintegration of aggregates might also occur when concretes are heated to 800 °C [43]. At the same time, dehydration went further at such an exposure temperature. It is therefore commonly agreed that concretes can only maintain a minor part of their original compressive strength after exposure to 800 °C [14]. The chloride diffusion tests could not proceed because the cracking is too severe and assessing the durability of concretes exposed to such a high temperature becomes meaningless.

Microcracking was found to be a major cause of deterioration when concretes were exposed to high temperatures, which was reported to initiate around $Ca(OH)_2$ crystals and then around unhydrated cement particles [44]. It is reasonable to assume that VA concretes are less susceptible to cracking during heating because VA can consume $Ca(OH)_2$ by further hydration. $Ca(OH)_2$ would decompose after exposure to above 400–600 °C, and the rehydration of dissociated $Ca(OH)_2$ becomes a detrimental cause of cracking, which is accompanied by a 44% volume increase [45]. It can be seen from test results that the addition of VA into binders could provide concretes with better residual properties after exposure to temperatures from 200 to 800 °C.

5. Conclusions

The strength and durability characteristics of high strength volcanic ash concrete (HSVAC) subjected to elevated temperature are presented based on experimental investigations. HSVACs are manufactured by incorporating 0–20% of volcanic ash (VA) as replacement of ordinary Portland cement (OPC) and with a constant of water-to-binder ratio (W/B) of 0.30. The HSVACs were subjected high temperatures ranging from 25 to 800 °C and their performance was assessed by residual compressive strength, resistance to chloride ion permeability, pore structure based on Mercury Intrusion porosimetry (MIP), deterioration indices, surface cracking, differential scanning calorimetry (DSC) and microstructural properties/interfacial transition zone (ITZ) (by means of microhardness testing). The following conclusions were drawn from the study:

1. The 28-day compressive strengths of HSVACs decreased with the increased replacement of OPC by VA.
2. In the range of 25–200 °C, an increase in strength was observed in HSVACs. From 200 to 400 °C, a decrease in strength was observed in HSVACs, which was 4–15% of the original strength. A severe loss in strength within the range of 32–48% was observed in the 400–600 °C temperature range. At 800 °C, all concretes deteriorated severely with residual strength ranged between 23% and 29%. The deterioration of strength at elevated temperature is due to the coarsening of the pore structure and increase in pore diameter. Generally the strength loss in HSVACs decreased with the increase of VA content compared with OPC concrete when the temperature was varied from 200 to 800 °C. The better performance of VA concretes as evidenced by no spalling or cracking, except for the development of hairline cracks, should be judged based on the slow rate of heating used in the tests.
3. Microhardness testing results revealed that the width of the ITZ increased after concretes were exposed to 200 °C. The increment was roughly by 42% and 14% respectively, for 0% and 10% VA concretes. However, no obvious increase in the width of the ITZ was observed in HSVACs with 20% VA. Tiny cracks along the transition zone might have appeared after the exposure to 200 °C, resulting in changes to the microhardness profiles. Significant losses in microhardness could only be observed in specimens exposed beyond 400 °C.
4. The increase in total porosity and the enlargement of the average pore diameter of hardened cement paste (hcp) became obvious when the exposure temperature was above 600 °C. However, a beneficial effect of higher VA content was demonstrated for temperatures at or above 600 °C.
5. The RCP test revealed that concrete durability deterioration commences at temperatures which are lower than those at which compressive strength deterioration commences.
6. Conclusively, HSVACs were found to be able to retain their strength and durability properties better at elevated temperatures (as confirmed from the residual strength, RCP values and microhardness characteristics) and

can be used in structures where there is a high risk of fire. However, an examination of durability should be made after the fire. This is important as the loss in durability may reduce the overall life of the HSVAC based structure.

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