Hydrophobic concrete using waste paper sludge ash

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ABSTRACT

The feasibility of using a low-cost super hydrophobic powder as water-resisting admixture or water-repellent surface coating for concrete has been investigated. The powder was produced from paper sludge ash (PSA), a by-product from the manufacture of recycled paper. The effect of hydrophobic PSA on workability, strength and transport properties, including sorptivity, water absorption, diffusivity, permeability and electrical conductivity is reported. Samples were prepared at water/cement ratio of 0.38, cured up to 28 days and conditioned at 50 °C to constant mass prior to testing. It was found that replacing Portland cement with 12% hydrophobic PSA reduced water absorption, sorptivity and conductivity by 84%, 86% and 85% respectively, with no major detrimental effects on hydration, strength and density. When used as a surface coating, the hydrophobic PSA reduced both absorption and sorptivity by 85–99% depending on the adhesive used. Samples surface coated with hydrophobic PSA showed excellent water repelling and self-cleaning characteristics.

1. Introduction

Ingress of water is the main cause of all the major physical and chemical degradation processes affecting concrete structures. Water may be the agent causing distress or it may allow the penetration of aggressive species that cause damage. Furthermore, excessive water penetration compromises the functionality of certain structures, e.g. basements, reservoirs and containment structures. Commonly used approaches to achieve durable watertight concrete involve increasing the density by using a low water–cement ratio, using supplementary cementitious materials and limiting crack widths using reinforcement or using surface protection technologies [1–4]. However, it is very difficult to eliminate water ingress because concrete is inherently porous and micro-cracked, it is often exposed to harsh environments and it is prepared using variable site practices.

An alternative approach to limit water ingress is through the use of integral water-resisting admixtures. These exist in solid or liquid form and can be classified broadly as: 1) materials that alter the surface tension or surface energy within pores and cracks to increase liquid contact angle and thereby resistance to absorption (i.e. water repellents, hydrophobers) or 2) materials that increase the resistance to water penetration under pressure by pore blocking resulting from deposition of solids via chemical reaction or removal from suspension (i.e. densifiers, permeability reducers, crystalline admixtures) [5–9]. Hydrophobic agents typically consist of fatty acids, vegetable oils, animal fats, wax emulsions, hydrocarbons, silanes and siloxanes and some proprietary admixtures that contain combinations of these. This approach has the

advantage over surface protection because successful application is not vulnerable to deterioration, does not require regular maintenance and can be used in structures where surface protection is difficult to apply.

A range of integral water-resisting admixtures are commercially available. Many claims have been made on their effectiveness, including the provision of permanent reduction in water transport, superior resistance to deterioration processes and increased service life. However, a recent review by the Concrete Society [8] found a distinct lack of independent data to substantiate these claims. Most of the available data is from manufacturers and much of the existing peer-reviewed research has examined generic materials rather than proprietary products. Constituents in these products are usually unknown and the mechanisms of how these admixtures work are also often not reported. This is especially true where the product is a mix of several components. Some water-resisting admixtures contain workability aids such as plasticizers that reduce the water/cement (w/c) ratio and produce a more dense concrete. Therefore, caution must be exercised when assessing these products because the improved performance may be due in part to the change in w/c ratio [8]. Some products appear to reduce water transport in low-grade porous concrete (high w/c, limited curing), but have limited effect on normal grade concrete [1,10]. Therefore these admixtures seem to do little to improve the performance of concrete beyond what can already be achieved by good mix design and construction.

Paper sludge ash (PSA) is a waste generated by the paper recycling industry. It is produced when dewatered waste paper sludge, a by-product of the de-inking and re-pulping of paper, is combusted to reduce waste volume and to produce energy. The combustion process is regulated in the EU and typically uses fluidised bed combustion at ~850 °C to 1100 °C. The UK produces ~125,000 tonnes/year of PSA, of

which 70% is used in low value applications such as land spreading, while the remaining 30% is typically sent to landfill [11,12]. The composition and properties of PSA vary according to the feedstock (dewatered waste paper sludge sent to the fluidised bed combustion unit) and combustion conditions, but it is highly alkaline with pH of 12–13 and is composed mainly of oxides of calcium, silicon and aluminium. The drive towards resource efficiency and reduced landfill has promoted research into the beneficial reuse of PSA.

Previous PSA research has focussed on hydraulic properties, pozzolanic reactivity and potential use as a supplementary cementitious material. For example, Pera and Amrouz [13] showed that calcining paper sludge at 700–750 °C produces a reactive pozzolanic material and this has been confirmed by others [14–17]. PSA can have cementitious properties; it reacts with water, sets and hardens. However, it has very high water demand due to high porosity, the developed strength are low for structural applications and the presence of free lime causes problematic expansion [14,18]. The presence of trace metallic aluminium in PSA has also been reported to cause swelling and expansion under alkaline conditions [17]. Shrinkage-induced cracking is also another potential problem. However, blending PSA with ground granulated blastfurnace slag improves strength development and alleviates some detrimental effects [14,18]. Fava et al. [19] also observed that a small increase in compressive strength can be achieved in mortar when 5% by weight of cement was replaced with PSA.

Recent research has demonstrated that PSA can be transformed into a super-hydrophobic powder using simple, low-cost processing, involving dry milling with stearic acid which acts as a surface functionalising agent [20]. Subsequent work has optimised the type and quantity of surface functionalising agent using a range of fatty acids and milling conditions [21] and optimal process produced a super-hydrophobic powder with a water contact angle of 153° [22]. Hydrophobicity results from the micro-particulate texture induced by milling and the formation of calcium stearate self-assembling monolayer that coats the fractured PSA surfaces.

The aim of this study was to evaluate the feasibility of using super-hydrophobic PSA powder as a partial cement replacement to improve the resistance of concrete to water ingress. Initial studies have also examined applying the super-hydrophobic PSA as a surface treatment to produce a water-repellent and self-cleaning coating. The influence of the super-hydrophobic PSA on a range of properties including absorption, diffusion, permeation and electrical conduction has been investigated and as far as we are aware, no published research has previously been reported on the use of PSA as an integral water-resisting admixture or surface coating. The novelty of the work is two-fold: transforming a waste product into a high value super-hydrophobic powder with very little processing and applying the hydrophobic powder to improve the performance of concrete.

2. Experimental

2.1. Materials

Paper sludge ash (PSA) was obtained from Aylesford Newsprint Ltd., a major UK newsprint manufacturer producing 400,000 tonnes per year of recycled newsprint from 500,000 tonnes of waste paper fibre. This generates about 70,000 tonnes of PSA every year. The PSA is mainly calcium aluminosilicate with a composition of 61.2% CaO, 21.2% SiO_2, 12.6% Al_2O_3, 2.8% MgO, 0.9% Fe_2O_3, 0.4% K_2O, 0.3% TiO_2, 0.2% SO_3, 0.1% P_2O_5 and 0.1% SrO as determined by X-ray fluorescence spectroscopy. The main crystalline phases determined by XRD are gehlenite ($Ca_2Al(AlSiO_7)$), calcite ($CaCO_3$), lime (CaO) and mayenite ($Ca_{12}Al_4O_{33}$). Scanning electron microscopy showed that the PSA is highly porous and comprises of loose agglomerates of smaller particles.

PSA was processed to form a hydrophobic powder by dry ball milling for 8 h using a 4 wt.% addition of stearic acid (Sigma Aldrich, 95% purity) as a surface functionalising agent. This was the optimum processing

conditions and produced a hydrophobic powder [22]. Dry milling was carried out using a 3 litre porcelain ball mill containing 19 mm diameter high density alumina milling media. The milling media to sample ratio was 5:1. Milling breaks down the PSA agglomerates and decreases the median particle size (d_{50}) from ~100 µm to 2–5 µm, but has no significant effect on mineral composition. The resultant powder had a water contact angle of 153° measured using the sessile drop method (Krüss Easy Drop tensiometer) and as a result is classified as super-hydrophobic. It is light grey in colour and has a specific gravity of 2.85.

Portland cement CEM I 52.5N complying with BS EN 197-1:2011 was used as the main binder in all samples, supplied by Hope Cement Ltd. Thames Valley siliceous gravel (<10 mm) and sand (<5 mm) were used as coarse and fine aggregates respectively. The gravel complied with BS EN 12620:2002 + A1 overall grading, and the sand complied with the BS 882:1992 medium grading. The gravel had a specific gravity of 2.48, moisture content of 1.3% and 24-h absorption of 2%. The sand had a specific gravity of 2.54, moisture content of 1.3% and 24-h absorption of 1.8%. Tap water was used as the batch water.

2.2. Samples

Three series of samples were prepared: Series I, cement pastes containing admixed hydrophobic PSA, Series II, cement pastes surface coated with hydrophobic PSA, and Series III, concretes containing admixed hydrophobic PSA. The free water/cement (w/c) ratio for all samples was fixed at 0.38. A low w/c ratio was selected so that the effectiveness of the hydrophobic PSA can be assessed on a dense concrete. Mix proportions for all 18 samples are shown in Table 1.

2.2.1. Series I

Series I consists of pastes containing 0, 2, 4, 8 and 16 wt.% replacement of cement with hydrophobic PSA. The pastes were prepared by dry mixing cement and hydrophobic PSA in a bowl mixer. Batch water was then added and mixed for 3 min. Disc samples were cast in steel moulds (100Ø × 50 mm) and compacted in two layers using a vibrating table until no significant air bubbles escaped the surface. There was a noticeable decrease in workability caused by the hydrophobic PSA powder, particularly at 8% addition and higher. Thus, the amount of vibration was adjusted to account for this. Compacted samples were covered with polyethylene sheet and wet hessian for the first 24 h, then de-moulded and cured in a fog room at 20 °C and 95% ± 5% relative humidity for 3 days. After curing, samples for transport testing were conditioned in an oven at 50 °C and 7% relative humidity until constant mass, which was taken to be achieved when consecutive 24-hour mass readings showed less than 0.02% difference. The purpose of this was to minimise the effect of sample moisture content on the measured mass transport properties so that a meaningful comparison can be made. The oven dried samples were then cooled overnight to room temperature in a desiccator containing silica gel prior to transport testing to ensure that their moisture content did not increase during cooling. Samples were taken out of the desiccator only when required for testing. Checks by weighing showed negligible mass change during cooling and storage prior to testing.

2.2.2. Series II

Series II consists of paste samples that were surface coated with hydrophobic PSA. Cylindrical samples were prepared as in Series I above, except that they were cast in plastic moulds (50Ø × 68 mm) and contained no admixed PSA. They were cured until the age of 3 days at 95% ± 5% RH, 20 °C and then conditioned to constant mass at 50 °C. After cooling to room temperature the samples were surface treated by applying a thin layer of adhesive, then covering the surface with hydrophobic PSA, followed by a gentle pressure to set the powder into the adhesive. The coating was left to cure for 24 h and excess hydrophobic PSA was removed with compressed air. The following adhesives were tested: a) wood varnish (Ronseal), b) high-strength polyvinyl acetate

Table 1
Samples and mix proportions.

Sample	Cement: kg/m³	Water: kg/m³	Free w/c	Hydrophobic PSA		Sand: kg/m³	Gravel: kg/m³	Curing: days	Notes
				%	kg/m³				
Series I									
P-0%	1434	545	0.38	–	–	–	–	3	
P-2%	1419	539	0.38	2	28.4	–	–	3	
P-4%	1405	534	0.38	4	56.2	–	–	3	
P-8%	1378	524	0.38	8	110	–	–	3	
P-16%	1327	504	0.38	16	212	–	–	3	
Series II									
P-0%	1434	545	0.38	–	–	–	–	3	No surface coating
P-0% V	1434	545	0.38	–	–	–	–	3	Coated with varnish only
P-0% V-PSA	1434	545	0.38	–	–	–	–	3	Coated with varnish and PSA
P-0% P	1434	545	0.38	–	–	–	–	3	Coated with PVA adhesive only
P-0% P-PSA	1434	545	0.38	–	–	–	–	3	Coated with PVA adhesive and PSA
P-0% C	1434	545	0.38	–	–	–	–	3	Coated with cyanoacrylate adhesive
P-0% C-PSA	1434	545	0.38	–	–	–	–	3	Coated with cyanoacrylate and PSA
P-0% E	1434	545	0.38	–	–	–	–	3	Coated with epoxy resin only
P-0% E-PSA	1434	545	0.38	–	–	–	–	3	Coated with epoxy resin and PSA
Series III									
C-0%	487	185	0.38	–	–	569	1057	3, 28	
C-4%	478	182	0.38	4	19.1	569	1057	3, 28	
C-8%	469	178	0.38	8	37.5	569	1057	3, 28	
C-12%	460	175	0.38	12	55.2	569	1057	3, 28	

(PVA) adhesive (EverBuild), c) a two-component epoxy resin based adhesive (Araldite) and d) cyanoacrylate adhesive (Loctite). For each adhesive, two samples were prepared: one with only the adhesive layer as control, and a second with adhesive and hydrophobic PSA. Preliminary trials where the hydrophobic PSA was simply mixed with the adhesive and then applied directly onto the surface did not produce a coating with good water-repelling characteristic. Thus, it is important to apply the adhesive as an interlayer to preserve the hydrophobicity of the PSA while providing adequate surface binding.

2.2.3. Series III

Series III consists of concrete samples containing 0, 4, 8 and 12 wt.% replacement of cement with hydrophobic PSA. Total aggregate fraction for all mixes was maintained at 65 vol.% and sand-to-total aggregate mass ratio was 0.35. Batch water was adjusted to account for aggregate absorption so that the target free w/c ratio was achieved. An entrapped air content of 1 vol.% was assumed in the mix design based on our previous measurements of similar concrete mixes. The mix design was carried out by absolute volume. Batching was done in a 30-litre capacity pan mixer by first dry mixing cement and aggregates for 60 s, followed by the hydrophobic PSA powder for 45 s. Finally, water was added and mixed for a further 3 min. Cubes (100 mm) and discs (100Ø × 50 mm) were cast in steel moulds and vibrated in three layers until no significant release of air bubbles was observed. Samples were then placed on a polythene sheet, covered with damp hessian and a further polythene sheet for the first 24 h. Samples were then de-moulded, weighed, wrapped in cling film and sealed in polythene bags and cured at 20 °C for 3 and 28 days. The cubes were used for density and compressive strength testing. Discs were conditioned at 50 °C, 7% RH until mass equilibrium following the same approach as in Series I for transport testing.

2.3. Workability, density and compressive strength

Workability of freshly mixed paste and concrete was determined using the slump test in accordance to BS EN 12350-2 [23] for concrete. For paste, the procedure was modified by using a mini slump cone which had a height of 75 mm and diameters of 40 mm (top) and 90 mm (bottom). The cone was filled in three layers, compacted with a tamping rod 25 times per layer and then carefully lifted. The average subsidence from the top of the cone was measured. Compressive

strength of hardened concrete was measured in accordance with BS EN 12390-3 [24] on 100 mm cubes at 3 and 28 days using four replicate samples and averaged. Samples were sandwiched between two 150 × 150 × 25 metal plates to ensure uniform loading at a rate of 0.3 MPa/s. Prior to strength testing, the density of each sample was determined by Archimedes's principle in accordance with BS EN 12390-7:2009 [25].

2.4. Degree of hydration

The degree of hydration of concrete was estimated by measuring the non-evaporable water content of equivalent paste samples after 3 and 28 days curing. Approximately 50 g from each sample was crushed, dried at 105 °C to constant mass to remove evaporable water, and heated to 1050 °C for 3 h. The non-evaporable water content was taken as the mass loss between 105 °C and 1050 °C, corrected for the loss on ignition of the cement and PSA. The degree of hydration was then calculated as the ratio of the non-evaporable water content per gram of cement to the amount at complete hydration, which was assumed to be equal to 0.23 g/g for ordinary Portland cement based on the classical work of Powers and Brownyard [26].

2.5. Visual assessment of hydrophobicity

The susceptibility of the samples to wetting was assessed in a simple qualitative manner by placing droplets of water on the surface and visually inspecting them over time. In another experiment, drops of black ink were placed on the sample. The sample was then tilted to allow the ink to roll off. Photographs were taken before and after to compare any differences in resistance to staining. The amount of staining seen on the sample was used as a qualitative indicator of self-cleaning and ability to repel liquids.

2.6. Sorptivity, O_2 diffusivity and O_2 permeability

The main focus of the research was to evaluate the effect of the super-hydrophobic PSA on the ability of cement-based materials to absorb and transmit water by capillary suction. This was carried out by placing disc samples (top trowelled face) on two Perspex rods in a tray of deionised water to a depth of 2–5 mm above the exposed surface

at room temperature (21 ± 1 °C). Prior to that, the circumference of each sample was sealed with two layers of waterproof tape to prevent side absorption and to ensure unidirectional flow. The amount of water absorbed with time was measured to the nearest 0.01 g by weighing at regular intervals up to 72 h. The water level in the tray was maintained at 2–5 mm above the exposed surface throughout. The tray was covered to prevent sample drying. Care was taken to avoid condensation falling onto the sample. Sorptivity (g/m²min^0.5) was calculated according to the classical unsaturated flow theory [27] by plotting the absorbed water per unit flow area against square-root of time, and determining the slope of the best-fit line. Six to ten mass readings taken during the first 24 h were used to draw the best-fit line. The coefficient of regression of the least squares fit was always greater than 0.98.

Concrete samples from Series III were also tested for oxygen diffusion, oxygen permeation and electrical resistivity. The diffusion test was carried out by placing samples in a cell with the top trowelled surface exposed to a stream of oxygen and the bottom cast face to a stream of nitrogen at equal pressure. The sample was fitted into a silicone rubber ring placed in a diffusion cell and the circumference of the sample was sealed by applying a lateral confining pressure of 0.57 MPa to prevent side leakage. The gasses were allowed to counter diffuse through the sample and the oxygen concentration in the nitrogen stream was monitored using a zirconia analyser. When a steady-state condition was reached, the oxygen concentration and flow rates were recorded to calculate intrinsic diffusivity (m²/s) according to Fick's first law of diffusion.

Oxygen permeability was determined by placing the sample in a cell similar to the one used for diffusion, but with the top face exposed to pressurised oxygen and the bottom face to atmospheric pressure. A pressure gradient was generated by applying oxygen at input pressures of 0.05, 0.15 and 0.25 MPa above atmospheric pressure. At each applied pressure, flow was allowed to stabilise and the steady-state outflow rate was measured using bubble flow meters. The apparent permeability at each pressure gradient was calculated according to Darcy's law for compressible fluids and the intrinsic permeability (m²) was determined by applying Klinkenberg's correction for gas slippage. Transport tests were carried out in four replicates per mix. Detailed descriptions of the test procedures are available elsewhere [28].

2.7. Absorption and electrical conductivity

On completion of the 72-h capillary rise test, concrete samples were fully immersed in deionised water and placed in a vacuum desiccator for 2 h. The vacuum was then released to allow ambient air pressure to force water in. Subsequently, samples left fully immersed in water for a further 40 days were surface dried and weighed. Absorption was calculated as the mass of water absorbed from the start of the pre-conditioned state (50 °C oven dried) divided by initial mass, expressed as a percentage.

Subsequent electrical conduction testing was carried out by clamping samples between two brass plates connected to an LCR data-bridge. A generous amount of a salt-free electrode gel was applied to ensure good electrical contact between the sample and electrodes. Electrical resistance was then measured at an alternating current frequency of 1 kHz to reduce polarisation effects. The readings typically stabilise within 1 min of connection. Three readings were taken per sample at three consecutive minutes and averaged. Electrical conductivity was then calculated from the resistance and the sample dimensions. Four replicate samples were tested per mix.

2.8. Air content

The air content of concrete samples from Series III were obtained by scanning the sample with a flat-bed scanner to produce a digital image of the cross-section and applying image analysis to measure the void area fraction. Disc samples were split using a diamond rotary saw. The cross-section (~100 × 50 mm) was then surface treated to increase contrast and facilitate segmentation of the air voids. This involved grinding with silicon carbide paper starting from a coarse grit of 80, followed by a grit of 120 and 500 at 70 rpm for 2 min per grit size. The flat ground surface was then cleaned with acetone in an ultrasonic bath to remove dust and slurry from the voids and then dried at 40 °C for 2 h. Two thin coatings of black ink were then applied in perpendicular directions using a permanent marker and allowed to dry. A white talcum powder was then spread on the surface and gently pressed into voids with a flat glass slide. Excess talcum powder was wiped away with the edge of a razor blade. Samples were then scanned with a flatbed scanner at 1200 dpi resolution (20 μm pixel spacing). Scanning was carried out in greyscale with the same settings applied to all samples. Images were cropped to exclude any damaged edges or large irregular voids caused by aggregate pull-outs. Finally, the air voids were segmented by referring to the brightness histogram, which shows two characteristic peaks representing the talcum powder-filled voids and the surrounding black painted background. A threshold was set at the mid-point value between peaks to produce a binary image, from which the area fraction of the segmented voids was calculated.

3. Results

3.1. Workability, density, compressive strength and degree of hydration

Fig. 1 shows the variation in slump with the addition of the super-hydrophobic PSA powder and it can be seen that workability decreased significantly with increasing PSA content. Both paste and concrete mixes became considerably stiffer as the amount of PSA increased. There appears to be a strong linear relationship between slump and PSA content, with a coefficient of regression of 0.99 for Series I and 0.95 for Series III. Slump decreased at a greater rate for the concrete samples. Nevertheless, the samples were compactable and did not show any signs of honeycombing on the cast surface.

Results for density, compressive strength and degree of hydration are presented in Table 2. Note that the standard error was calculated by dividing the standard deviation (σ) by the square root of number of replicates (n). All three properties were not significantly affected within the range of PSA content studied. However, there was a noticeable decrease in density at 12% PSA. Samples cured for 28 days exhibited greater strength and degree of hydration than samples cured for 3 days. There were significant increases in strength and degree of hydration between 3 and 28 days and the hydration and strength values achieved appear to be typical for the mix.
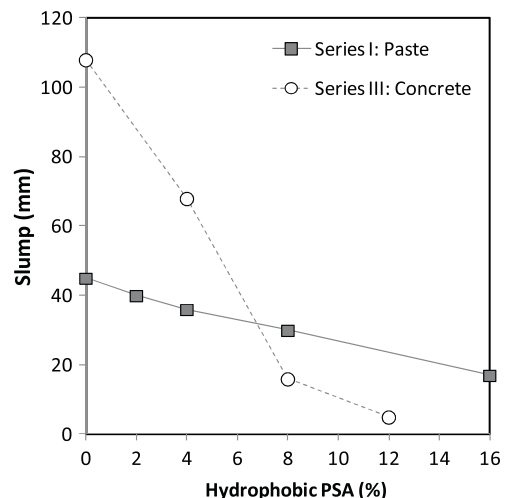

Fig. 1. Effect of admixed hydrophobic PSA on slump.

Table 2
Density, compressive strength and degree of hydration of concrete containing admixed hydrophobic PSA. Results for density and strength are average of four replicates and standard errors ($=\sigma/\sqrt{n}$) are shown in brackets.

PSA (%)	Density (kg/m³)		Compressive strength (MPa)		Degree of hydration	
	3 days	28 days	3 days	28 days	3 days	28 days
0	2368 (1.6)	2354 (6.4)	47.5 (0.5)	64.5 (0.9)	0.57	0.67
4	2359 (3.8)	2354 (4.3)	47.1 (0.4)	64.0 (0.6)	0.58	0.67
8	2358 (1.8)	2362 (2.9)	50.0 (0.5)	65.0 (0.3)	0.58	0.68
12	2337 (1.5)	2338 (3.0)	49.4 (0.9)	61.7 (0.6)	0.59	0.68

3.2. Visual assessment of hydrophobicity

Fig. 2 shows the results of the ink-staining tests. Fig. 2a shows the samples immediately after black ink was dropped on the surface. Note that there is a slight depression at the centre of each sample due to the plastic mould used during casting. All samples containing super-hydrophobic PSA coating exhibited interesting behaviour in which the ink droplets form beads on the surface that immediately roll to the centre, merging into one large bead and settling at the lowest point. This is shown more clearly in Fig. 3. However, the control samples and samples with adhesive only coatings did not exhibit this behaviour. Fig. 2b shows the effect of tilting the sample to allow the ink to roll off the surface. It can be seen that the control sample stained immediately because the ink was rapidly absorbed. Samples with adhesive only coatings displayed varying amounts of staining. Samples with adhesive and PSA coatings were highly hydrophobic and the ink bead simply rolled off with virtually no staining. These samples therefore exhibited a self-cleaning property.

Fig. 4a to d shows the effect of admixed hydrophobic PSA on the surface wetting characteristics of concrete samples. For consistency, the

images were taken 30 s after placement of water drops on pre-conditioned samples. Increased PSA content resulted in less wetting and hydrophobicity can be observed. No significant difference was observed between samples cured for 3 and 28-days. Further trials produced a hydrophobic surface on the control mix (C-0) either by forming a layer of PSA powder on the top surface of freshly compacted concrete, or by placing a layer of PSA evenly in the base of the mould and pouring fresh concrete on top. The latter produced a more positive result (Fig. 4f) and it was observed that water beads would run off an inclined surface without wetting the sample. Sprinkling PSA powder on top of fresh concrete was less effective (Fig. 4e), probably because it did not form a continuous surface coating.

3.3. Absorption and sorptivity of pastes

Fig. 5a shows the cumulative water absorption plotted against square-root of elapsed time for paste samples containing admixed hydrophobic PSA (Series I). The data show typical behaviour of a rapid initial water uptake that gradually decreases with time. Samples containing increased additions of PSA absorbed significantly less water by capillary action. The control sample showed a 12.4% increase of initial mass due to absorption and reached near saturation after 72 h. In comparison, the paste containing 8% PSA had a 3.1% gain in mass and the sample containing 16% PSA only increased in weight by 1.6% (Fig. 5c).

Fig. 5b shows the corresponding values for PSA coated samples (Series II). The amount of water absorbed was greatly reduced as a result of the surface coating. The mass of the coated samples increased by an average of 0.82% compared to 12.4% for the non-coated sample. The control samples with the adhesive only coating were also very effective at reducing water absorption. However the absorption of samples with adhesive and hydrophobic PSA coating were consistently
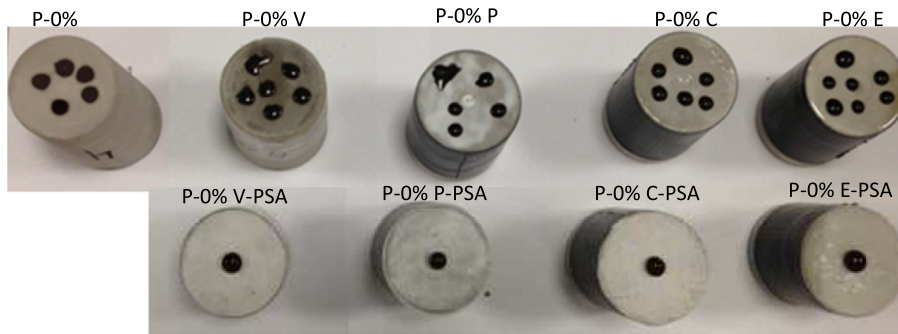
a) *Droplets of black ink placed on sample*
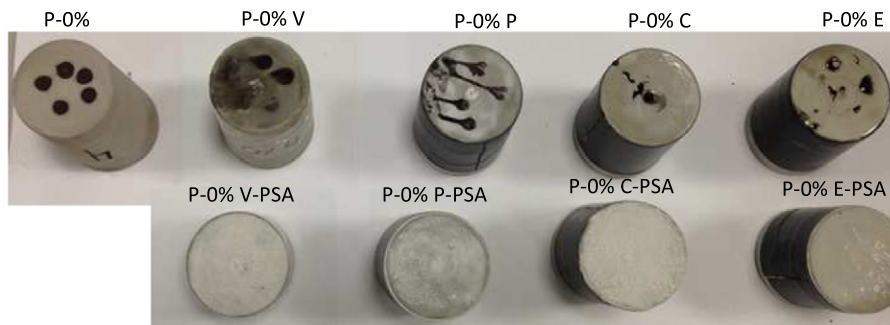
b) *Sample titled (to the left) to remove ink and residual staining is observed*

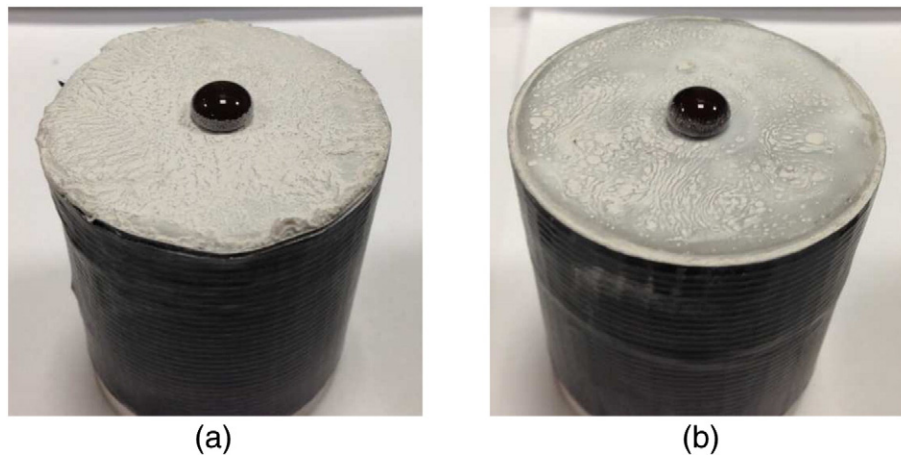Fig. 2. Visual assessment of hydrophobicity by ink staining. Samples have a diameter of 50 mm.

Fig. 3. Close up photo showing a single large ink bead forming on the centre of samples from Series II coated with hydrophobic PSA: a) P-0% C-PSA, b) P-0% P-PSA.

lower (by 10–26%), indicating that the super-hydrophobic PSA and adhesive layer provided the best performance (Fig. 5c).

The sorptivity coefficients for all samples from Series I & II are shown in Fig. 5c. The sorptivity indicates the rate at which water is absorbed via capillary action and this reduced as the percentage of PSA increased.

Replacement of 2% PSA produced a 62% reduction in sorptivity compared to the control. The corresponding decreases in sorptivity are 72% (for 4% PSA), 83% (for 8% PSA) and 92% (for 16% PSA). The most effective coatings are those based on the super-hydrophobic PSA and either cyanoacrylate or epoxy resin, both of which reduced absorption
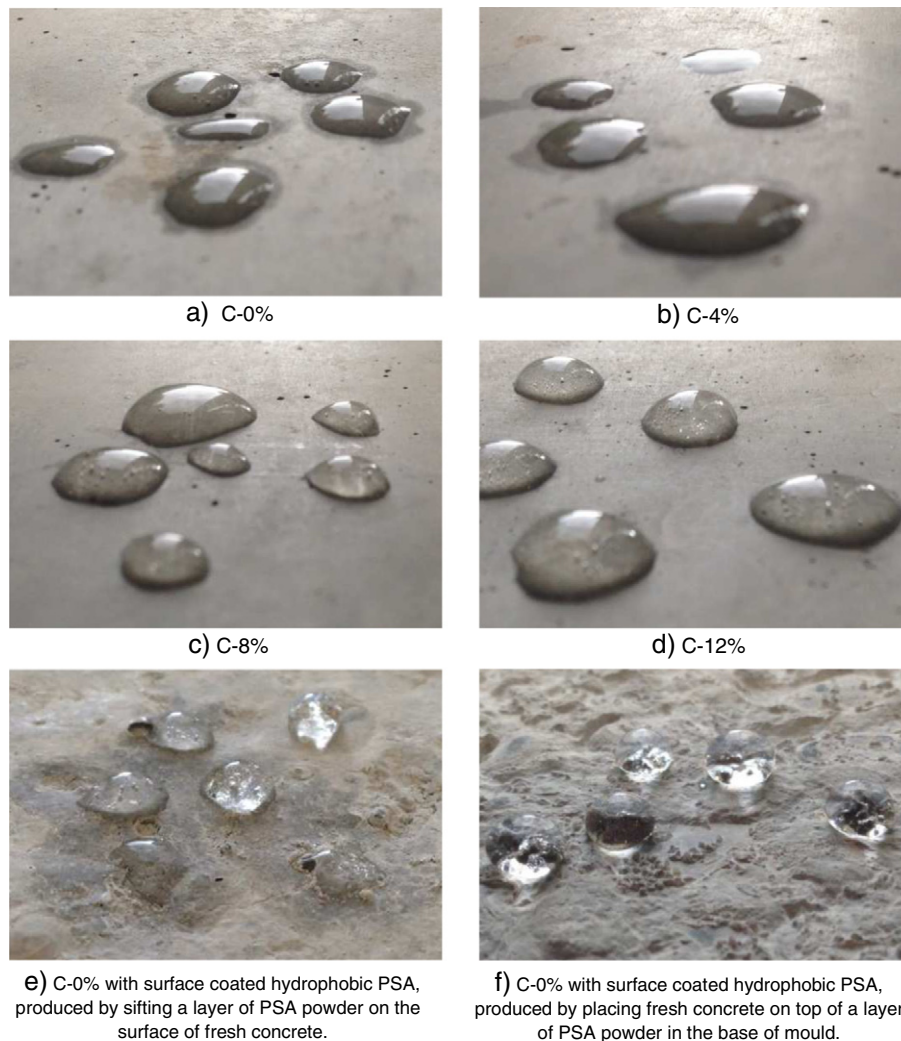

a) C-0%

b) C-4%

c) C-8%

d) C-12%

e) C-0% with surface coated hydrophobic PSA, produced by sifting a layer of PSA powder on the surface of fresh concrete.

f) C-0% with surface coated hydrophobic PSA, produced by placing fresh concrete on top of a layer of PSA powder in the base of mould.

Fig. 4. Photographs showing the effect of hydrophobic PSA on the wetting characteristics of concrete samples. For consistency, images were taken 30 s after placement of water droplets on pre-conditioned samples.
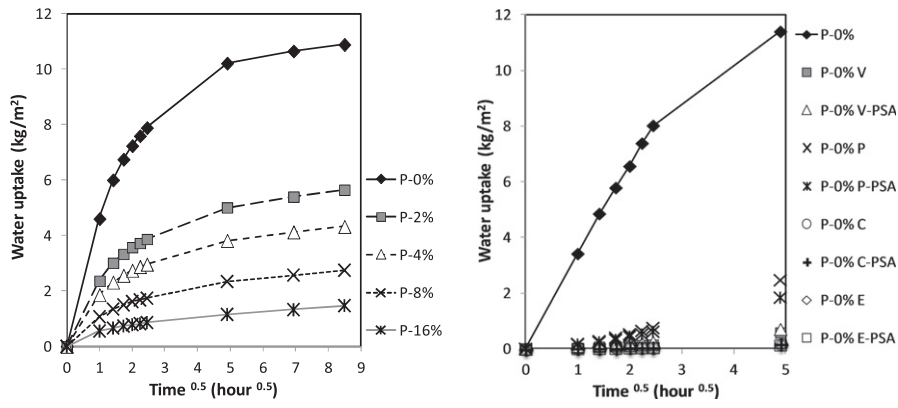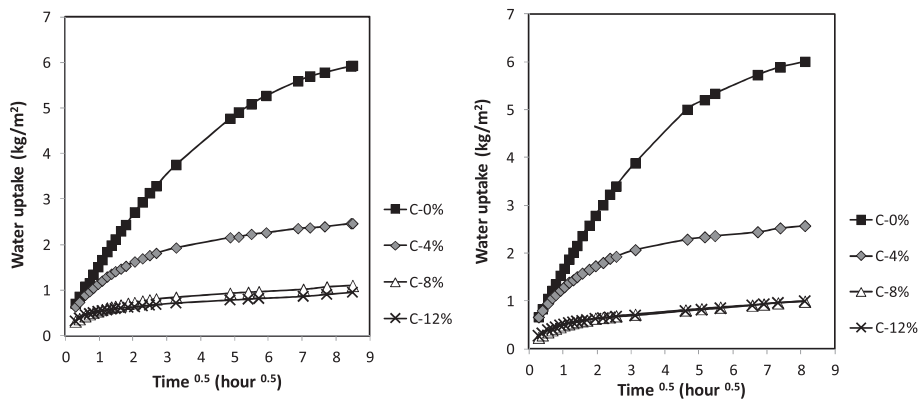
a) Series I (pastes containing admixed PSA)

b) Series II (surface coated pastes)
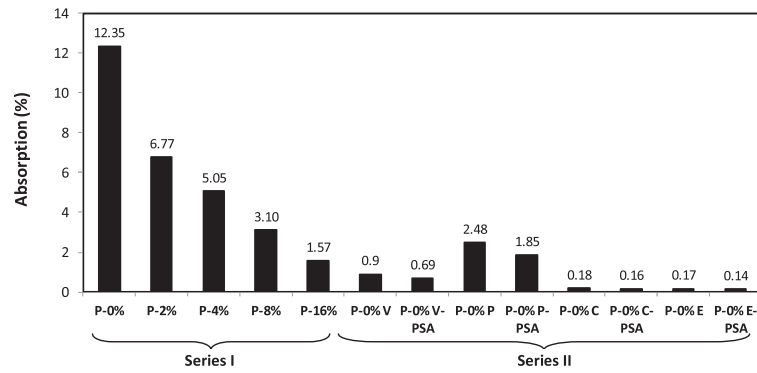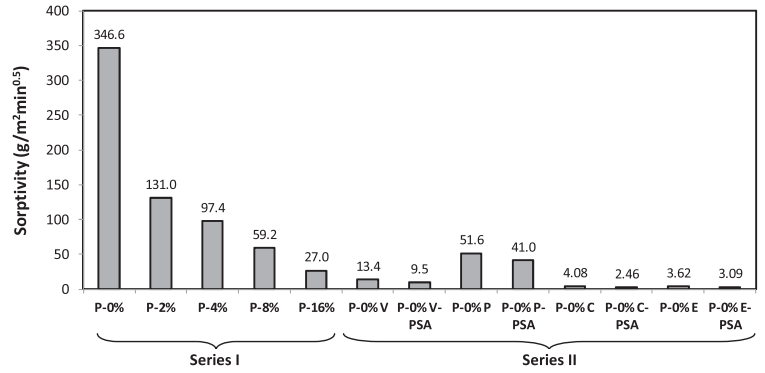
c) Sorptivity and absorption

Fig. 5. Cumulative water uptake plots, sorptivity and absorption for cement pastes containing admixed PSA (Series I) or surface coated PSA (Series II).

a) Series III (3d)

b) Series III (28d)

Fig. 6. Cumulative water absorption plots for concretes containing admixed PSA.

and sorptivity by more than 99% compared to the control. The least effective adhesive coating was the PVA (85% reduction in absorption and sorptivity).

3.4. Transport properties of concretes

Fig. 6 a and b shows the cumulative water uptake for 3-day and 28-day cured concrete samples from Series III plotted against square-root of elapsed time. Water uptake is initially rapid and gradually decreases with time. The control was nearly saturated at the end of the experiment (72 h). Absorption decreased with PSA content. At 4% PSA, absorption was reduced by over 55% and 12% PSA reduced absorption by 83–84%. The difference between 8% and 12% PSA was negligible, suggesting that 8% may represent an optimal addition. Note that the water uptake in concrete samples is approximately half that of the pastes (Fig. 5a). This is expected because of the diluting effect of the non-sorptive aggregates present in the concrete samples. Nevertheless, the reductions in water uptake due to PSA were similar for pastes and concretes.

Table 3 shows the averaged sorptivity, diffusivity, permeability, electrical conductivity and absorption for concretes from Series III. In Fig. 7, the transport coefficients are normalised by the respective control value and plotted against PSA content to highlight trends. Note that the error bars indicating variability within replicates are small and not visible in most cases. The results show that sorptivity, absorption and electrical conductivity decreased with increase in PSA content. Replacement at 4% PSA decreased sorptivity by 50%, while replacement at 12% PSA decreased sorptivity by 83–86% relative to the control. The decrease in electrical conductivity ranged between 26% and 85%. The effect of PSA on oxygen diffusivity and oxygen permeability was less consistent. The lowest diffusivity and permeability occurred at 8% PSA for both curing ages, but there was some increase at 12% PSA. Nevertheless, the change in diffusivity and permeability are small compared to sorptivity and resistivity.

At the end of the 72-hour capillary rise test, the water absorption of samples containing PSA were 58–84% lower than the control (Table 3). As an additional test, all samples were fully immersed in water and placed under vacuum for 2 h. They were then left immersed for another 40 days and weighed to recalculate absorption. Results show that all samples experienced further mass gain. However, the measured absorption for the concrete samples containing super-hydrophobic PSA remained much smaller than the control. In all cases, the super-hydrophobic PSA remained effective under conditions of vacuum saturation and long-term immersion. Increasing PSA content enhanced the ability of concrete to resist water ingress. This suggests that the admixed

super-hydrophobic PSA can withstand significant amount of hydrostatic pressure.

3.5. Air content

An assumption was made that all samples were well compacted despite the variability in slump. This was based on visual assessment of the external surface quality. However, there is a possibility that this assumption is incorrect and that poor compaction may have influenced transport properties. This raises the question of whether the observed trends are indeed due to the effect of the super-hydrophobic PSA. Therefore, it was necessary to carry out further testing to determine if samples were affected by poor compaction and to what extent. Representative binary images showing the segmented air voids and calculated air content on the cross-section of concrete samples are presented in Fig. 8. It was found that air content only varied between 1.2% and 3.9%, but there was a clear indication of an increase with PSA content with a regression coefficient of 0.99. This correlates well with the results from the slump test. Therefore, samples containing super-hydrophobic PSA are not as well compacted as the control samples. This increased air content is expected to influence the measured mass transport properties and the significance of this will be discussed later.

3.6. Effect of very high PSA dosage

A further trial was completed in which a paste sample was prepared containing 50 wt.% super-hydrophobic PSA. Initially, the paste was prepared at w/c ratio of 0.38, but the mix was too dry. The water content was gradually increased up to w/c ratio of 0.70 but the mix remained dry. On closer examination, it was observed that many small agglomerates containing trapped mix water had formed. The water can be released if the agglomerates are squeezed, but the water agglomerates would subsequently reform. The hardened paste formed was very porous, lightweight with a density of about a third of the reference sample and weak. Fig. 9a shows a cross section of the paste containing 50% PSA at w/c 0.7. Due to the large porosity and pore sizes, the sample does not exhibit hydrophobicity on its surface. In contrast, it had a high capacity for absorption and showed a 27% mass increase in the first hour, rising to 37% after 24 h.

When a drop of water is placed and allowed to roll on a layer of super-hydrophobic PSA, the powder attaches on the droplet and forms a film that eventually coats the entire surface of the droplet. The water is contained and effectively trapped within the PSA film. This effect is shown in Fig. 9b. The droplet can be transferred onto a piece of paper without wetting it. However, breaking the PSA film releases the trapped water, wetting the paper. This interaction can be explained by

Table 3

Transport properties of concretes from Series III pre-conditioned at 50 °C. Results are average of four replicates and standard errors ($= \sigma/\sqrt{n}$) are shown in brackets.

a) 3-day cured						
Sample	Sorptivity ($g/m^2 \cdot min^{0.5}$)	O$_2$ diffusivity ($\times 10^{-8}$ m^2/s)	O$_2$ permeability ($\times 10^{-17}$ m^2)	Conductivity (10^{-3} S/m)	Water absorption (%)	
					After 72 h capillary rise	After 2-h vacuum + 40 day immersion
C-0%	153.4 (4.8)	9.05 (0.09)	11.4 (0.68)	5.09 (0.33)	5.11 (0.06)	6.07 (0.08)
C-4%	76.5 (1.6)	9.27 (0.09)	10.1 (0.93)	3.76 (0.07)	2.13 (0.03	5.18 (0.14)
C-8%	30.7 (1.7)	7.40 (0.13)	9.92 (0.73)	3.65 (0.02)	0.95 (0.06)	4.32 (0.22)
C-12%	21.4 (0.9)	7.63 (0.14)	15.5 (0.61)	1.53 (0.13)	0.81 (0.03)	3.29 (0.06)

| b) 28-day cured						
Sample	Sorptivity ($g/m^2 \cdot min^{0.5}$)	O$_2$ diffusivity ($\times 10^{-8}$ m^2/s)	O$_2$ permeability ($\times 10^{-17}$ m^2)	Conductivity (10^{-3} S/m)	Water absorption (%)	
					After 72 h capillary rise	After 2-h vacuum + 40 day immersion
C-0%	151.4 (4.0)	8.53 (0.12)	15.7 (1.41)	6.03 (0.05)	4.91 (0.11)	5.76 (0.05)
C-4%	77.1 (3.4)	8.44 (0.15)	12.6 (1.29)	4.33 (0.28)	2.13 (0.11)	4.51 (0.15)
C-8%	29.3 (1.2)	6.38 (0.09)	12.3 (0.55)	0.90 (0.06)	0.80 (0.04)	2.62 (0.05)
C-12%	26.0 (0.5)	7.14 (0.11)	17.6 (1.06)	1.17 (0.11)	0.82 (0.02)	2.87 (0.05)

a) 3-day curing

b) 28-day curing
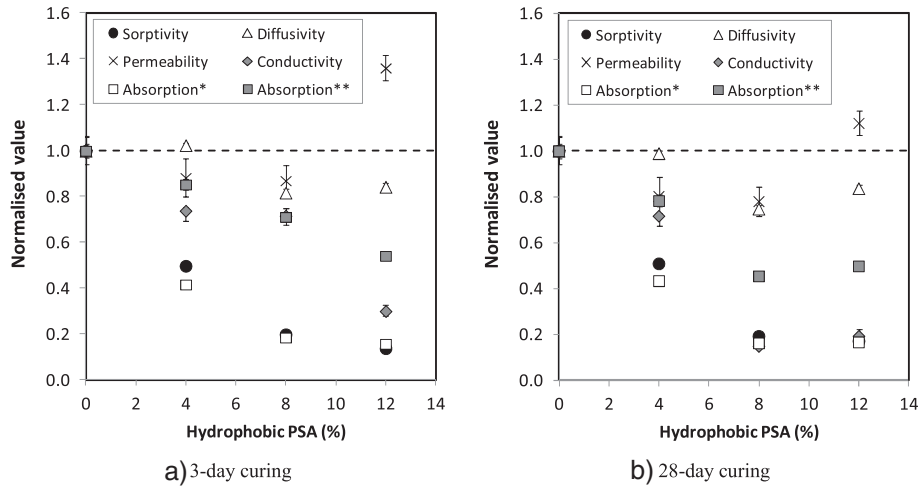
Fig. 7. Influence of admixed hydrophobic PSA on sorptivity, diffusivity, permeability, conductivity and accessible porosity of concrete from Series III. Results are normalised to the control sample (0% PSA). Note that "Absorption*" was calculated after 72-h capillary rise, while "Absorption**" was calculated after a further 2-h vacuum saturation + 40 day immersion.

the PSA particles having both hydrophobic and hydrophilic properties, with the latter attaching to water leaving the hydrophobic surface facing outward in air. This allows water droplets to be coated with a hydrophobic PSA film.

A similar phenomenon is likely to occur when mixing concrete with PSA. A portion of the mix water is 'locked in' by the hydrophobic powder and prevented from wetting the ingredients. This increases with PSA content. As a consequence, the amount of free water available is reduced causing the marked fall in workability (Fig. 1) and degree of compaction (Fig. 8) observed. At very large hydrophobic PSA contents, the powder stabilises and entrains air bubbles formed during mixing. This produces a highly porous and lightweight but weak material as shown in Fig. 9a. An air entraining effect has also been observed using other hydrophobic admixtures [8,29,30].

4. Discussion

The mass transport properties in cementitious materials are influenced by a host of factors including w/c ratio, binder type, admixtures, aggregate content, type and duration of curing, degree of hydration and the test method employed. These factors should be taken into consideration when assessing and comparing the effectiveness of the super-hydrophobic PSA against other options for reducing water transport. Transport properties are also greatly influenced by the moisture content and distribution in the sample at the time of testing. Therefore, it is important that samples are conditioned for an extended period of time prior to testing. By the end of the conditioning, samples will have reached a fairly consistent low moisture content so variations in measured transport cannot be attributed to sample moisture condition. Oven-drying at 50 °C is a relatively extreme drying condition and it

will have induced microcracking as shown in Wu et al. [31]. Therefore, the performance of the super-hydrophobic PSA used in this research was evaluated under a rigorous and demanding set of test conditions.

The increase in air content due to the super-hydrophobic PSA could influence transport properties and so the significance of this must be examined. Air voids can increase or decrease transport properties, with the net effect dependent on the transport mechanism under consideration and the moisture content of the air voids. Air voids facilitate gaseous transport because they are interconnected via capillaries in the cement paste. However they also reduce the capacity for water absorption because they generate lower suction compared to capillary pores. Empty air voids also act as non-conductive inclusions and so reduce electrical conductivity. For example, it has been shown that air contents of 2–4% can increase gaseous diffusivity and permeability by up to a factor of two relative to the control [32]. A reduction in sorptivity and conductivity is only noticeable at air contents greater than 4% (Fig. 3 of Ref. [32]). Since all the samples tested in this study had air contents less than 4%, it is unlikely that the observed decrease in sorptivity and conductivity with increasing PSA content (Fig. 7) is caused by air voids. Furthermore, the magnitude of the decrease in sorptivity and conductivity measured is far greater than what can be attributable to the effect of air voids [32].

Most concrete structures in service are unsaturated and so ingress of water and water-borne aggressive agents is largely controlled by capillary absorption. This is the major transport process relevant to many exposure environments and degradation mechanisms and so its reduction is the key to enhancing durability. The addition of super-hydrophobic PSA was able to produce large decreases in both the rate (sorptivity) as well as the amount of water absorbed, but without having any negative effects on strength and other properties. When used as partial
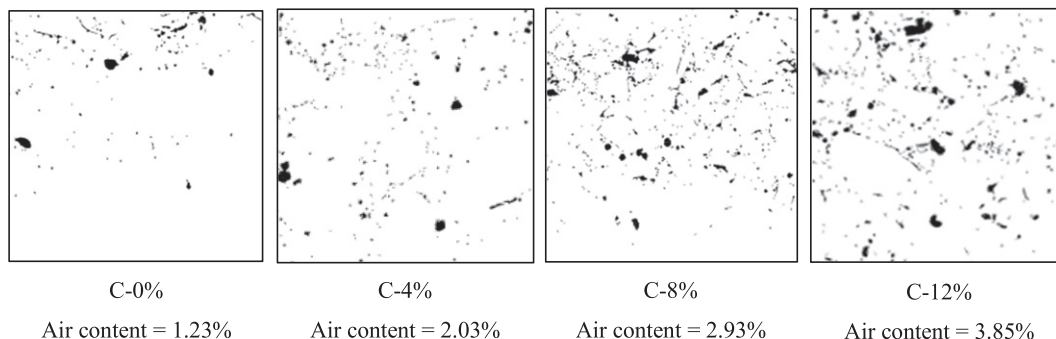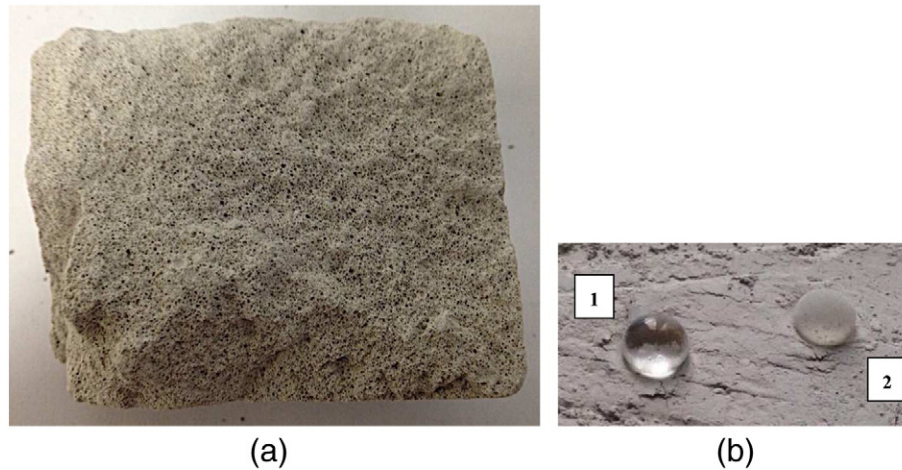

C-0%	C-4%	C-8%	C-12%
Air content = 1.23%	Air content = 2.03%	Air content = 2.93%	Air content = 3.85%

Fig. 8. Binary images showing segmented air voids from cross-sections of concretes from Series III. Air content increased with addition of PSA. Field of view of the images is ~45 × 45 mm.

Fig. 9. a) Cross-section of paste with 50% admixed hydrophobic PSA. Sample was very porous, lightweight and weak. b) Droplet 1 placed on PSA, while droplet 2 was rolled and coated with a thin film of PSA.

cement replacement at 12%, the hydrophobic PSA decreased sorptivity and absorption by up to 86% and 84% respectively. When used as a surface coating, it decreased both sorptivity and absorption by up to 99%. Furthermore, electrical conductivity was decreased by up to 85%. This is because electrical conduction occurs through ions in the pore solution, so the measured conductivity is dependent on the water content. This explains why conductivity follows the trend of sorptivity and absorption (Fig. 7).

A w/c ratio of 0.38 was used in this study so that the performance of the super-hydrophobic PSA could be assessed on a dense concrete. This is significant as it has been known that some integral water-resisting admixtures are only effective on porous matrixes [1,10]. Most available studies on water-resisting admixtures and surface treatments have been carried out on samples with relatively high w/c ratio, typically at ~0.5 or higher. Nevertheless, it would be interesting to compare results. Aldred et al. [10] tested a proprietary hydrophobic admixture on concretes at w/c ratio of 0.6 and 0.4, cured in a fog room up to 28 days, then oven-dried at 40 °C prior to testing. They observed that the admixture decreased water absorption by ~67–78% relative to the control. The reduction in water transport was more pronounced in concretes of higher w/c ratio, as well as under conditions of limited curing and greater drying. Justnes [29] reported the use of seven vegetable oils as hydrophobic admixtures at dosages of 0.5–1.5% cement weight. Tests were carried out on mortars at w/c ratio of 0.5 that were cured for 28 days, then dried at 50 °C. It was observed that capillary absorption after 3 day immersion was reduced by 15–66% depending on the type of admixture used. Lanzón and García-Ruiz [30] tested the effect of six waterproofing admixtures: calcium stearate, zinc stearate, sodium oleate, silicones and hydrophobic polymer at dosages up to 2 wt.% of sample. It was observed that absorption after 90-minute immersion was reduced by 57–86% at the highest dosage.

de Vries and Polder [33] tested nine commercially available hydrophobic surface treatments including silanes and silane/siloxanes in various solvents. The concretes had w/c ratio of 0.5 and were cured for 3 days, dried for 6 weeks at 20 °C, 65% RH and then surface treated and tested. It was observed that the surface treatments reduced 24-hour water absorption by 60–98%. In another study, Almusallam et al. [34] evaluated ten commercial surface coatings that consisted of acrylic, polymer emulsion, epoxy resin, polyurethane and chlorinated rubber coatings. The base concrete samples (0.45 w/c ratio) were moist cured for 14 days and then dried at 70 °C for 24 h prior to surface coating and testing. They observed a wide variation in the performance of the coatings, even those within the same generic type. Overall, the surface coatings decreased water absorption by 28–96% and decreased sorptivity by 4–94% relative to the control.

Medeiros and Helene [35] tested six commercial surface treatments including water repellents (silane/siloxane), acrylic, polyurethane coating and double systems (water repellent + acrylic coating). The base concrete had a w/c ratio of 0.52 and was wet cured for 91 days, and then dried at 60 °C to constant mass prior to surface treatment and testing. The coatings reduced sorptivity by 73–98%. In another study, Christodoulou et al. [36] tested concrete cores from a 43-year old motorway bridge that were surface treated with a commercial silane-based product. The surface treatment had 12–20 years of service and the concrete mix composition was unknown. Their results showed that the treated cores had lower sorptivity by 8–73% relative to the control cores. When the control cores were treated with a new silane coating, sorptivity decreased by up to 88%.

Comparing the percentage reduction in water absorption or sorptivity in the literature with the result on the performance of the super-hydrophobic PSA suggests that it is on par with all, if not better than most of the products tested. Perhaps another way to assess the super-hydrophobic PSA is to compare the measured sorptivity against those of well cured high-performance concretes with low w/c ratio. The data from studies where samples were conditioned at 50 °C prior to testing shows that sorptivity ranged from 35–85 $g/m^2 \cdot min^{0.5}$ for concretes with w/c ratio 0.3–0.4 that were wet cured for up to one year. This includes data from high-performance concretes containing microsilica (7.5–10%) or metakaolin (10–20%) [37–40]. Comparing this to our data (Table 3, Fig. 5c) suggests that the super-hydrophobic PSA is able to decrease sorptivity beyond the level that can be achieved by low w/c ratio, prolonged curing or incorporation of reactive pozzolans.

These findings are promising as the use of super-hydrophobic PSA would lead to an overall improvement in concrete durability. The super-hydrophobic PSA decreases water absorption, but has no influence on gaseous transport and therefore the rate of evaporation. Therefore, it is expected that the moisture content of concrete will decrease over time, leading to dryer interior and increased resistance to many deterioration mechanisms that require water as the reaction medium. The benefits associated with restricting water absorption include decreasing ingress of water borne aggressive agents such as chlorides and sulphates, reducing the amount of freezable water, limiting reaction rates and reducing leaching. The decrease in electrical conductivity is beneficial from the point of view of reducing steel corrosion rates. The use of super-hydrophobic PSA allows a reduction of cement content in concrete while maintaining or improving performance. This is beneficial in the context of sustainability, which is often considered in relation to the embodied energy/carbon of cements and whole-life impacts of concrete structures.

The influence of the admixed super-hydrophobic PSA on the hydration kinetics of cement and microstructural development is not fully understood and research is on-going in this area. Nevertheless, current results suggest that replacement of 8% by weight of cement with the super-hydrophobic PSA has no detrimental effect on the degree of hydration, compressive strength and density (Table 2). At 12% PSA, a slight reduction in strength and density was observed. However, there was no retardation in degree of hydration suggesting that the decreases in strength and density are due the higher air content as shown by image analysis (Fig. 8). We envisage that this could be overcome through the use of compatible superplasticizers to compensate for the loss of workability. Thus, a greater replacement of cement by super-hydrophobic PSA may be possible.

A fundamental question is the mechanism by which the admixed super-hydrophobic PSA influences transport properties. There are several possibilities. The PSA may be reactive, forming additional hydration products that fill void spaces and increase the density of the microstructure. At 12% cement replacement, the volume of PSA is substantial, about 2% of the sample and therefore it may also act as pore-blocking inert filler. If these are the main mechanisms, the PSA would cause a reduction in the volume, size and connectivity of the pore structure. The results suggest that this is unlikely because there were little changes in the measured strength, oxygen diffusivity or oxygen permeability. A more plausible mechanism is that the PSA arranges itself within the microstructure or bonds with the hydration products in a way that produces hydrophobic surfaces within the pore structure. Thus, the volume and structure of the capillary pores are not so much affected, but the surface characteristics, in particular the solid–liquid contact angle, are altered. This will decrease capillary suction that affects liquid transport, but not gasses, which is consistent with the results reported.

More research is required to determine the long-term effects of the admixed super-hydrophobic PSA and surface coating on the properties of concrete. Further work is needed to establish its performance on a larger range of concretes with different w/c ratio, curing and condition regimes, and to establish its effectiveness in porous and cracked systems. Further studies should be carried out to verify the influence it has on chloride ingress and binding, carbonation, time to damage initiation and deterioration rates. It would also be interesting to complete more rigorous testing on the resistance to externally applied water pressure. Research on optimising the surface coating process and understanding its long-term durability is also required.

5. Conclusions

This study examined the influence of a super-hydrophobic powder derived from waste paper sludge ash (PSA) on a range of properties of pastes and concretes at water/cement ratio of 0.38 and cured for up to 28 days. The aim was to determine the feasibility of the super-hydrophobic PSA as an integral water-resisting admixture or as water-repellent surface coating for concrete. The following conclusions can be drawn:

- Super-hydrophobic PSA is very effective at reducing both the amount and rate of capillary water absorption. Partial replacement of cement with 12% super-hydrophobic PSA decreased water absorption in concrete by 83–84% and decreased sorptivity by 83–86% relative to the control concrete prepared at the same water/cement ratio, curing age and conditioning regime. Electrical conductivity was decreased by up to 85% because of the reduced internal moisture content. These effects increased with an increase in PSA content.
- Gaseous diffusion and permeation were not significantly affected by the super-hydrophobic PSA.
- Concretes containing super-hydrophobic PSA showed significantly lower absorption even after vacuum saturation and 40-day immersion in water. This indicates that the super-hydrophobic PSA can resist hydrostatic pressure to some extent.

- A decrease in workability was observed, but no major detrimental effects on compressive strength and hydration occurred for cement replacements of up to 8%. At 12% PSA, a slight reduction in strength and density was observed due to an increase in air content. At very high replacements (50%), the super-hydrophobic PSA showed an air entraining effect which produced a lightweight, porous but weak material.
- When used as a surface coating, the super-hydrophobic PSA was able to reduce both absorption and sorptivity by 85–99%, depending on the adhesive used. Samples with surface coated PSA showed excellent water repelling and self-cleaning characteristics.
- Comparison with data from the literature suggests that the performance of the super-hydrophobic PSA is similar/better than many water-resisting admixtures and surface treatments. The super-hydrophobic PSA is also able to decrease sorptivity beyond the level that can be achieved by a low w/c ratio, prolonged curing or incorporation of reactive pozzolans.

The study concludes that super-hydrophobic PSA has significant potential as an admixture or surface coating to enhance the resistance of concrete to water ingress, and therefore against a range of deterioration mechanisms. This offers a high-value application route for a waste material that can potentially enhance the durability and sustainability of concrete structures.

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