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Hydrophobic concrete using waste paper sludge ash

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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

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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