Hydrophobe VI
6th International Conference on Water Repellent Treatment of Building Materials
Aedificatio Publishers, 23 - 32 (2011)

Influence of Blended Cements on the Performance of Water Repellent Agents

M. A. Kargol, U. Mueller, A. Gardei and B. Meng
Federal Institute for Materials Research and Testing, Division VII.1 - Building Materials, Unter den Eichen 87, 12205 Berlin, Germany

Abstract

Ingress of moisture and harmful ions (e.g. chloride, sulfate) into cementitious materials is one of the major factors in defining their durability. Modifications of building materials by targeted deposition of surface functional agents that make the surface hydro- and/or oleophobic aim to minimize moisture and ion ingress, and thus extend service life of the cement based structures. Water repellent and easy-to-clean coatings for inorganic substrates have gained strong attention during the last few years and various formulations based on silicones or alkylpolysiloxanes have been developed. Cementitious building materials are highly complex systems with many components and changing properties in the course of a building's service life. The interactions between the chemical agents and the cement based materials depend on many factors. The chemical properties of the material substrate appear to be the most important but in the context of their influence on the functionality of silanes and/or siloxanes these characteristics have not been well understood yet. The aim of this study was to evaluate the effect of different blended cements on water repellent agents' performance. Two organosilicon compounds were applied on fresh blended cements containing limestone (L), fly ash (F), slag (S) and trass (T), and investigated in terms of their functionality. The surface properties of functionalized blended cements were studied based on wettability, i.e. contact angle measurements, before and after exposure to artificial and natural weathering. The first results indicate that slag and trass more distinctly affect the water repellent surface performance after aging.

Keywords: hydrophobic surfaces, wettability, impregnation, blended cement, silanes

1 Introduction

Surface protection systems are applied to building materials in order to increase their service life, change their appearance or enlarge their performance range. These systems usually consist of chemical agents able to penetrate into the pore space of concrete by capillary suction and interact with hydrated cement particles [1, 2]. A wide range of silicon-based chemicals have been used for decades in construction applications, and are now the great part of new research and product development. These materials usually consist of low-molecular weight silanes or mixture of silanes and siloxanes, applied either diluted with organic solvents, undiluted or as aqueous systems [3].

Due to water and/or oil repellent properties of alkyl-polysiloxanes obtained by hydrolyzis and polycondenstation reactions inside the building material, the impregnation with alkyl-alkoxysilanes represents one of the applicable method of reducing the water uptake without remarkably changing the water vapour permeability.

Though the development of the water repellent agents from the formulation side is quite straightforward, the knowledge concerning the effectiveness, the functionality and durability of these agents on building material substrates is more erratic. In particular, cementitious building materials are highly complex systems with many components and changing properties in the course of a building's service life. It is important to underline that a successful treatment depends not only on the product itself and its application but also on the substrate to which it is applied and the conditions to which it is exposed.

The majority of experience concerning the efficacy of water repellents on cementitious materials is gained from Portland cement while knowledge with regard to the interactions of blended cement with water repellent agents is minimal. Production of Portland cement is an energy intensive process and releases a very large amount of green house gas to the atmosphere [4]. Industrial by-products such as fly ash, silica fume or blast furnace slag have been increasingly applied as clinker replacement or mineral addition in cement [5-7]. Production and utilization of these materials can result in economical, ecological and technical benefits, e.g.: energy savings, reduction of the hydration heat, environmental protection or improved durability to various types of chemical attack. For that reason, the blended cements are becoming increasingly important on the market and many cement manufactures nowadays produce more blended cement (CEM II and CEM III) than Portland cement (CEM I).

This paper presents the results of a study dealing with the effect of water repellents on hardened blended cement pastes. The performance and durability of selected silane-based hydrophobic products was assessed on prepared previously blended cement pastes by testing their wettability and impact of artificial and natural aging.

2 Experimental

2.1 Materials

A total of five cement based pastes was prepared using an Ordinary Portland Cement (CEM I 42.5 R, OPC) and limestone filler (L), fly ash (F), slag (S) and Rhenish trass (T). The water/cement (w/c) ratio was adjusted to 0.45, i.e. the pozzolanic components were included in the calculation of 'c'. First, the pure cement paste was prepared by mixing of CEM I 42.5 R with water for 5 minutes in a mortar mixer. The obtained cement paste was cast into cylindrical metal moulds in size of 50 mm in diameter and 200 mm in height. All specimens were demoulded after one day of curing under a plastic cloth in a laboratory environment. Then, the samples were placed in sealed plastic boxes above distilled water (to ensure a high humidity) and stored in a climate room at constant temperature of 21 ± 3 °C for 28 days. For blended cement pastes preparation, first the CEM I 42.5 R was homogenized for 6 h with 30 weight % of limestone (OPC L), fly ash (OPC F), trass (OPC T) and 60 weight % of slag (OPC S) with respect to the OPC content and then water was added. Further procedure was the same as for OPC paste. After demoulding, drying (at 21 °C and 60 % of RH) and cutting (to get the cylindrical specimens of 40 mm in height) the formwork surface was used for treatment and testing. The cement specimens were subdivided into four groups and all measurements were carried out on untreated (Reference), treated and aged samples. Each test was done twofold.

2.2 Treatment

After preparation as described in 2.1, two sets of cement specimens were treated with two products, i.e. a silane based hydrophobic product commercialised as an anti-graffiti product (AG) and n-octyltriethoxysilane used as model system (MS). The anti-graffiti silane was purchased from Evonik while n-octyltriethoxysilane from Merck. The two hydrophobic agents were applied on the hardened cement paste by means of a brush at ~23°C and ~50 % of RH after cleaning the surfaces with compressed air. The n-octyltriethoxysilane was applied twice. The interval between successive treatments was at least 14 days. The specimens were stored for at least 14 days at ~23°C and ~50 % of RH before carrying out further tests. For each hydrophobic product, three cement slabs were used. Untreated cement samples were exposed to the same conditioning before they were examined as reference samples.

2.3 Methods

The contact angles measurements of treated cement specimens were performed by using an OCA-20 Contact Angle System from Data Physics Instruments to evaluate the hydrophobic and oleophobic surface properties. Water and 1-bromonaphthalene drops were placed at six different points of one specimen, and the contact angle was measured immediately after droplet placing at about 21 °C. The average values of measured contact angles have been used for data interpretation. During this test, the size of liquid drops was kept constant at about 3 µl. The measurements were performed on treated and aged samples (artificially and in the outdoor conditions).

To simulate the deterioration process caused by sunlight and water on the samples treated with hydrophobic products an accelerated aging test was performed. All treated and untreated samples were placed in a weathering chamber and artificially aged for a total of 8 weeks. The cement specimens were positioned in a climate chamber with a slight slope of about 3 degrees to the horizontal. The aging procedure was performed in accordance to the standard EN 13687-2 [8] (UV radiation and humidity) with a cycle of 5 h 35 min of UV light exposure at 60 °C followed by 25 min of water condensation at 25 °C. Prior to experiment, the samples were conditioning at ~23°C and ~50 % of RH. The colour changes were examined before and after exposure by means of a Minolta Spectrophotometer CM-508d on untreated and treated surfaces of the cement samples with a 50 mm diameter measuring area. The chromatic values of L*, a*, and b* were averaged from four measurements on three cement samples.

Simultaneously to artificial aging, an outdoor weathering experiment was carried out for 6 months (from May 2010 to October 2010). The intention was to determine the resistance of hydrophobic products to solar radiation and atmospheric conditions. The untreated and treated cement slabs were fixed in plastic holders and placed on the roof in a vertical position and exposed to urban environment. Every three months the effect of natural weathering on the cement samples was evaluated by measuring colour changes. Moreover, after six months of outdoor exposure the hydro- and oleophobic properties of the treated surfaces were verified by means of contact angle measurements.

3 Results and discussion

Since the wettability of the surface is directly related to the contact angle between a liquid drop and a solid material, the static contact angles were determined by using water as a liquid. Moreover, 1-bromonaphthalene was used for the evaluation of surface oleophobicity. The water contact angles (WCA) for the cement surfaces treated with the two products, i.e. AG and MS together with error bars are given in Figure 1 including results for the aged sample specimens. The values of contact angles for untreated samples (Reference) were below 40° and are not presented here. A higher value of the contact angle (θ) indicates the good hydrophobic nature of the surface, while low values indicate the non-hydrophobic surface. The solid surface is perfectly wetted for $\theta = 0°$ and it is hydrophilic for $\theta < 90°$ while it is hydrophobic for $\theta \geq 90°$ [9]. The sufficient hydrophobization is achieved at contact angles greater than 90° [10]. The obtained data clearly evidence that after treatment the cement surfaces were highly hydrophobic regardless of the applied product and cement paste composition. This hydrophobic effect seemed to be slightly more pronounced for cement specimens treated with the MS product (before aging), especially for cement paste containing fly ash, OPC F-MS (Figure 1, right).

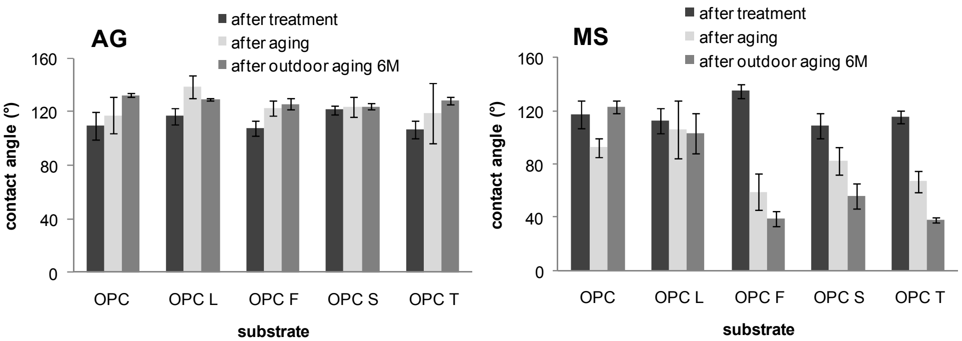

Figure 1: Water contact angles with error bars for different cement pastes treated with AG and MS products (after treatment, after aging and after 6M of outdoor aging)

After the artificial aging experiment, the water contact angle measurements were again performed on the cement specimens treated with different products. As shown in Figure 1, there is no influence of the aging carried out in a weathering chamber on cement specimens treated with the AG product. There was even an increase in the hydrophobicity observed after aging. The similar results were obtained after the outdoor weathering experiment. Here, the data for water contact angles are presented after six months of outdoor exposure. Again, it was noticed that for all aged cement pastes treated with the AG product, the surface was highly hydrophobic regardless the composition of the substrate.

The results obtained after artificial aging for cement specimens treated with n-octyltriethoxysilane (MS product) showed that the static water contact angles were significantly reduced comparing to samples before aging. Most of the treated cement pastes lost their good surface performance and only pure cement paste (OPC) and paste containing limestone (OPC L) preserved hydrophobic properties. The applied pure silane was not sufficiently resistant to UV radiation and humidity exposure. The water contact angle values obtained after the outdoor weathering test were similar to artificially aged samples. The treated cement pastes containing fly ash, slag and trass seemed not to be resistant to natural weathering conditions.

Hydrophobicity of the surface is frequently associated with oleophobicity, the affinity of the substrate for oils. The oil contact angles (OCA) of 1-bromonaphthaleine measured after treatment and aging experiments are given in Figure 2. As expected, for the AG product based on fluoroalkylsilane, the presence of the fluoroalkyl groups enhanced significantly the oleophobic character of the surface. All cement specimens were highly oleophobic, both after treatment and after aging, regardless of the conditions of exposure. Similar results were obtained previously for measured water contact angles. The presence of fluorine atoms in the commercial products giving their characteristic low surface free energy that makes them water- and oil-repellent is an explanation. In addition, the C-F bond is very stable towards visible and UV-light that make fluorinated materials more resistant to degradation [11]. The low OCA value after artificial aging for the cement paste containing trass can be caused by inhomogeneous distribution of the product at the surface. In contrary, all cement specimens treated with the MS system attained lower values of the OCA (Figure 2, left). After treatment, the cement surface seemed to be slightly oleophobic; however exposure to in- and outdoor aging caused a decrease in OCA values.

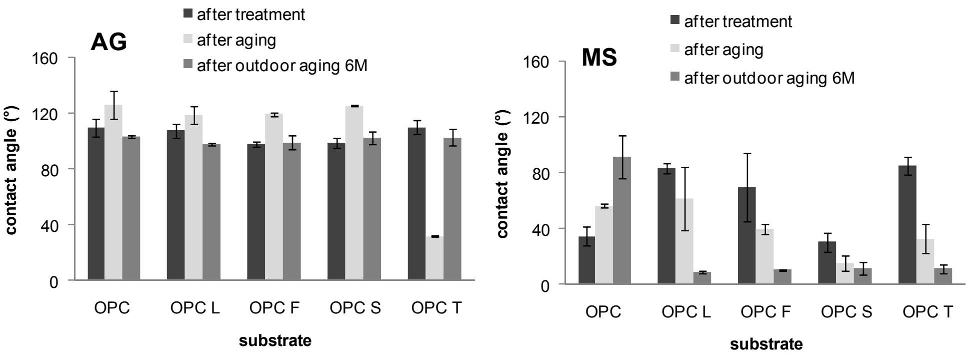

Figure 2: Oil contact angles with error bars for different cement pastes treated with AG and MS products (after treatment, after aging and after 6M of outdoor aging)

The durability of the treated cement surfaces was also reflected by results of colorimetric measurements on samples exposed to accelerated artificial aging and natural weathering. For all cement specimens, the total colour variations were calculated before and after treatment with the AG and MS products. In Figure 3, the changes in the lightness L* are presented for untreated cement specimens (Reference) and treated ones after the artificial aging and after outdoor weathering test of three and six months of duration, respectively. L* parameter represents the surface lightness and varies from black (0) to white (100). In general, the untreated cement specimens (Reference) after the artificial aging are less resistant to lightness changes. The negative value of lightness is attributed to the darkening of the surface. The applied treatment improved the appearance of cement surfaces for both products. However, this preferable colour performance is more pronounced for the cement specimens treated with the MS product. Application of the AG product caused an increase in the lightness difference regardless the composition of the substrates. A higher L* value may indicate a higher degree of efflorescence (whiteness or lightness). After the artificial aging experiment a crystalline deposit of salts on the cementitious surface was observed for samples treated with the AG product. It is important to mention that all aging experiments were carried out on the relatively small specimens resulting in damage of the samples, e.g. cracks, and thus influencing the obtained results.

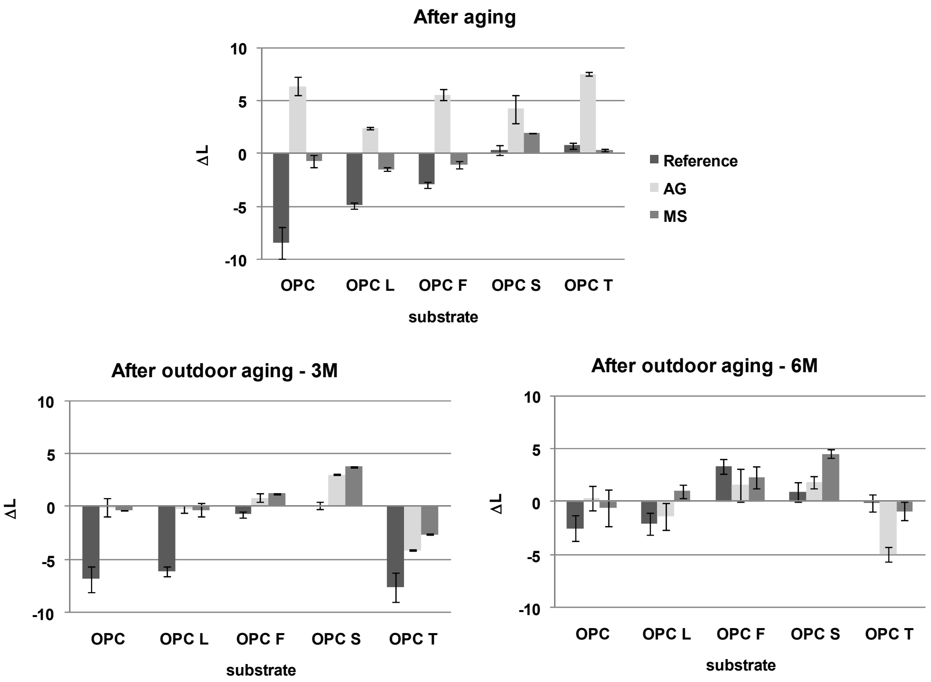

Figure 3: Difference of lightness with error bars for untreated and treated cement pasted after artificial and natural aging of three and six months

After treatment with the AG and MS products, the red-green chromatic parameter a* (positive for red and negative for green colours) remained almost unaltered. For the yellow-blue chromatic parameter b* (positive for yellow and negative for blue colours) more pronounced variations were observed.

The effect of natural weathering conditions on the untreated and treated cement specimens was evaluated every three months again by measuring the colour changes. The cement surface appearance for untreated and treated specimens was different depending on the applied product and substrate composition. Apart from cement paste containing fly ash and slag, untreated cement samples showed greater darkening of the surface than treated cement specimens. The darkening was more pronounced for cement paste containing trass and treated with the AG product. However, over the months an increase in the lightness difference and the other colour components (a* and b*) was observed.

4 Conclusions

The data acquired in this study have indicated that the performance of surface treatment based on two agents varies more with the exposure conditions than the cement paste composition. The results showed that the surface wettability, both hydrophobicity and oleophobicity was not very dependent on the substrate composition, especially for cement specimens treated with the anti-graffiti product.

The exposure of treated cement specimens to artificial and natural weathering resulted in colour variations despite of very good oleophobic performance of the surface. The treatment with the anti-graffiti agent and its highly oleophobic surface after aging has not prevented the colour changes. In contrary, the MS product lost its highly hydrophobic properties after exposure to aging but performed better for example in terms of the lightness difference.

Cement pastes containing fly ash, slag and trass seemed to more distinctly affect the water repellent surface performance after aging.

References

[1] S. Giessler, E. Just, R. Störger, Easy-to-clean properties – Just a temporary appearance? Thin Solid Films (502), (2006), pp. 252-256

[2] J. G. Dai, Y. Akira, F. H. Wittmann, H. Yokota, P. Zhang, Water repellent surface impregnation for extension of service life of reinforced concrete structures in marine environments: The role of cracks, Cement and Concrete Composites (32), (2010), pp. 101-109

[3] I. J. Vries, R. B. Polder, Hydrophobic treatment of concrete, Construction of Building Materials (11), (1997), pp. 259-265

[4] V. M. Malhotra, Introduction: Sustainable Development and Concrete Technology, ACI Concrete International (24), (2002), pp. 22

[5] Z. Wu, T. R. Naik, Properties of concrete produced from multicomponent blended cements, Cement and Concrete Research (32), (2002), pp. 1937–1942

[6] V. M. Malhotra, Properties of fresh and hardened concrete incorporating ground, granulated blast-furnace slag. In: V.M. Malhotra, Editor, Supplementary cementing materials for concrete, CANMET, Canadian Government Publishing Centre (1987), pp. 289–333

[7] P. Chindaprasirt, P. Kanchanda, A. Sathonsaowaphak, H.T. Cao, Sulphate resistance of blended cements containing fly ash and rice husk ash, Construction and Building Materials (21), (2007), pp. 1356–1361

[8] EN 13687-2 Products and systems for the protection and repair of concrete structures – Test methods – Determination of thermal compatibility – Part 2: Thunder-shower cycling (thermal shock) (2002)

[9] M. Zielecka, Methods of contact angle measurement as a tool for characterization of wettability of polymers, Polymers (49), (2004), pp. 327-332

[10] M. Alvarez de Buergo Ballester, R. Fort Gonzales, Basic methodology for the assessment and selection of water-repellent treatments applied on carbonatic materials, Progress in Organic Coatings (43), (2001), pp. 258-266

[11] J. Scheerder, N. Visscher, T. Nabuurs, A. Overbeek, Novel, water-based fluorinated polymers with excellent antigraffiti properties, Journal of Coatings Technology and Research (2), (2005), pp. 617-625