IMPACT OF HYDROPHOBIC MODIFICATIONS ON MICROSTUCTURE AND MICROMECHANICS OF CEMENTITIOUS MATERIAL

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Abstract: *This paper compares recent methods of internal hydrophobization of cementitious composite by silicon-based solutions and a crystalline admixture used as the alternation of external coatings. The study focuses on the overall hydrophobic performance of the admixtures as well as on their impact on the microstructure and micromechanical properties. Results contained in this paper show both positive influence of the admixtures and limitations with respect to their micromechanical performance measured by nanoindentation.*

Keywords: Cementitious composite, Hydrophobization, Crystalline admixture, Nanoindentation

1. Introduction

The majority of corrosion degradation process is related to water propagation through pores in structural material. Thus, with the development of new materials, modern concept in the field of civil engineering is to increase the structure durability by limiting the penetration of the water. Formerly, the materials have been modified by external hydrophobic coatings. Based on the latest researches, other problems can result from the approach, such as degradation of the coating layer itself and the sustainability of the material properties. In order to lower the degradation of the hydrophobic agent, internal hydrophobization is taken into consideration as a possible solution. As such, crystalline admixtures were recently used in cementitious composite. In some cases, this method was considered ineffective thanks to the lack of the knowledge about the admixture behavior on the micro-scale and its microstructural interaction within the material. This paper deals with both water-repellent performances of the selected hydrophobic admixtures as well as with their micromechanical influence assessed with nanoindentation.

2. Theoretical background

2.1. Hydrophobization

The hydrophobic coatings used for external treatment of cementitious materials are typically silicon based water solutions, in which silanes and siloxanes oligomers are represented. Their reaction is closely discussed e.g. in Hrbek et al. (2016). The simplification of their evolution can be described as poly-condensation process leading to the development of a thin layer of silica polymeric chain connected to the surface over the hydrogen-oxygen bonds. The degree of polymer chain depends on the presence of the "free" water during the condensation process and on the type of silicon based solution. This also results in decrease of water necessary for

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hydration of cement. In case of external hydrophobization, the formed coating is subjected to the degradation, mostly caused by the de-bonding of the hydrogen-oxygen link.

The crystalline admixtures are usually described as active chemicals coupled with very fine sand and cement as an admixture used as a sealant in waterproof concrete structures. The hydrolytic active particles, in reaction with water or the calcium-silica-hydrate (C-S-H) gel, increase the C-S-H density or produce the crystalline deposits that block the penetrating water into the material. This provides the material with calcium silicate crystals that integrally bond with the cement paste and enclose the pores and the cracks. This reaction can thus be, based on the space and water available, repeated over the service life of the structure. By now, this method of waterproofing provides the largest resistance to penetrating water under pressure.

2.2. Micromechanical properties and nanoindentation

The nanoindentation, as a method of micromechanical testing, is today a widely used technique of direct estimation for elastic and plastic properties of the material on the microscale. Its principle is based on the measurement of penetration of a rigid tip into the material surface. Standardly, load-penetration depth diagrams of small material volumes allow determination of mechanical properties of small material volumes, such as hardness H or reduced modulus E_r as

$$H = \frac{P}{A_c} \qquad\qquad E_r = \frac{1}{2\beta} \frac{\sqrt{\pi}}{\sqrt{A_c}} \frac{dP}{dh} \qquad\qquad (1)$$

where P is the maximum load, A_c is the projected contact area of the tip, dP/dh is the unloading stiffness, β is the geometrical constant. The reduced (combined) modulus can be used for calculation of Young's modulus with the knowledge of the material Poisson's ratio (Oliver and Pharr, 1992). Even though the method was found for homogeneous-like materials (metals, ceramics, etc.), it can be successfully used for microscopically heterogeneous material, such as cementitious composites by using a method of statistical grid indentation coupled with deconvolution of the material phase distributions (Constantinides et al., 2006, Němeček et al., 2013, Leal Da Silva et al., 2014).

3. Methodology of testing

3.1. Sample description

The investigated samples were made of a cementitious composite mixture consisting of CEM I-42,5R and micro-silica as binders, fine aggregate perlite (with diameter lower than 200 μm) and 3M glass micro-bubbles as filler. The water cement ratio of the mixture was 0.35 and the Sika-Crete plasticizer (with ratio 0.12 to binders) was used to obtain an optimum workability.

The enhancement of the hydrophobic properties by use of sodium-methyl-siliconate (SMS) in SMS to binder weight ratio 0.10% to 0.15% was proved by previous research (Hrbek et. al., 2016). In this paper, substitution of 0.00%, 0.10%, and 0.20% of SMS solution were compared to specimens with the crystalline admixture used as a binder replacement of 0%, 1% and 2%, as recommended by the producer (Xypex). Samples were matured in water over the period of 28 days. Further sample labeling used in this work is HYFx.xx for samples with silicone based solution and XYPx.xx for Xypex crystalline admixture replacement, where x.xx indicates the SMS or Xypex to binder ratio, respectively.

3.2. Macro-scale hydrophobicity

The macroscopic properties of water repellence were tested on samples 40x40x160 mm. 28 days after the production short term water absorption was tested after specimens drying in 30°C for 3 days. Then, samples were placed on wetted linen by one surface and the increments of samples' weight were measured over the next 4 hours. In order to obtain the terminal dry weight, samples

were placed in 45°C for the next 14 days. Then, samples were saturated with water for 24 hours in a vacuum chamber under the pressure of 150 mbar, their weight gain was measured and the full saturation ratio with respect to their dry weight calculated.

3.3. Mechanical properties based on nanoindentation

The effect of hydrophobic alternation of the sample micromechanical properties was quantified by the change in distribution of reduced elastic moduli measured over large representative areas of the sample that were previously polished by a metallographic procedure to minimize their roughness. The indentation was performed with diamond Berkovich tip in several 20 by 20 indent grids with mutual indents' separation of 25 μm in ambient conditions (~21 $^{\circ}$C, ~20-40% r.h.). The linear loading lasting for 5 seconds with 0.4 mN/s loading rate was prescribed and maximum load of 2 mN was reached for all indents leading to the maximum penetration depth of 335±124 nm. The following constant holding of the force over 20 seconds allowed material for creep so the following unloading part, from which elastic material parameters are evaluated, can be supposed unaffected by a time-dependent process. The unloading again lasted for 5 seconds.

4.   Results

4.1. Macroscopic water absorption

Based on the data from Fig. 1a), the internal hydrophobization by silicon based solution exhibits lower short term absorption compare to crystalline admixture. Such effect can be explained by a lower level of saturation of near surface pores in the crystalline-modified sample during the measurement. In other words, the efficiency of the crystalline admixture is, unlike the silicon-based modification, water-supply and time dependent. In case of full saturation, as depicted in Fig. 1b), the SMS solution proved insufficient ability to repel water under pressure and the results may indicate de-bonding of the polymeric agent from the surface. As for the crystalline particles, the water-supply ensures sealing of the pores resulting in a rapid decrease of saturation ratio.
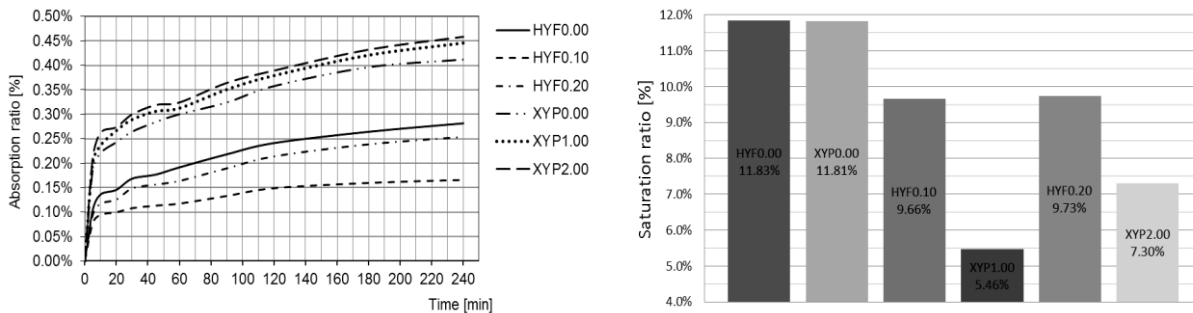

Fig. 1: Comparison of a) average short term absorption ratio and b) full saturation ratio

4.2. Micromechanical performance

Results presented in Fig. 2 show the probability density of reduced moduli merged from all measured positions, i.e. containing mechanical response from different microstructural phases. Based on the local and overall shifts in the histograms the effect of hydrophobic modification can be established. Clearly, the silicon based admixture interacts with other reactive components and shifts the phase stiffness towards lower or higher values (Fig. 2a). In the case of low concentration (HYF0.10) the reduced moduli of the main hydrated phases are lower compared to untreated samples. The possible reason for that is an altered reaction kinetics and the formation of more low-density C-S-H phase. In contrast, reduced moduli for the sample with higher SMS ratio (HYF0.20) and thus lower w/c ratio are shifted towards higher values. This can be explained by the reaction rate of the cement minerals, where fastly reactive tricalcium silicate

reacts with the water prior to other minerals which may lack water later. Their hydration products, ettringite and portlandite, exhibit higher stiffness corresponding to presented data. Further evolution of lower stiffness C-S-H phases then can be lowered due to the lack of water supply. The active particles in crystalline admixtures that are several tens of micrometers large are mostly dissolved in the mixture by the alkaline environment with partial integration to the matrix. In Fig. 2b, the presence of non-dissolved particles is indicated by a low stiffness (local peak bellow 10 GPa for the sample XYP 2.00). On the other hand, the low stiffness portion of the material in this case has a potential of a further reaction (not studied here). The lower concentration of the particles (XYP1.00) alters the reduced modulus in the least amount as compared to reference samples.
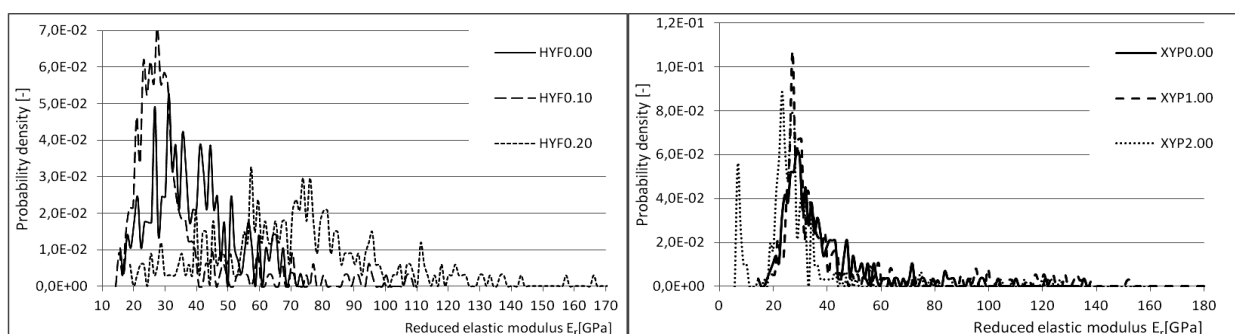

Fig. 2: Probability density of E_r – a) SMS solution, b) Xypex crystalline admixture

5. Conclusions

It has been shown that the crystalline admixtures can be used as internal hydrophobic agents similarly to silicon based solutions. They are highly efficient for surface hydrophobization in lower concentrations (Hrbek, 2016) and can be dispersed in the mixture also internally as shown in this paper. It was proved by micromechanical tests that the SMS admixture interacts with hydrating phases of cement and causes a shift in their stiffness. The conclusion provided here is based on a short term testing. A long term performance should be studied in the future. The crystalline admixture shows higher hydrophobic potential in under-pressure water intake. However, competing mechanisms of the admixture dissolution and pore sealing takes place in the microstructure which is again manifested by the shift in their micromechanical performance. Based on the short term studies an optimum replacement ratio of the crystalline admixture seems to be around 1% with respect to the binder.

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