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Interaction between wastewater microorganisms and geopolymer or cementitious materials: Biofilm characterization and deterioration characteristics of mortars

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ABSTRACT

This paper compares the biofilm formation during field exposure to real municipal wastewaters on geopolymer and copper-doped geopolymer mortar, with plain Portland cement and calcium aluminate cement as controls. The samples were submerged in a wastewater treatment plant at three different stages for 35 days (primary clarifier, activated sludge and final effluent), which led to diverse chemical and biological exposure conditions due to the different organic load of the three environments. The deterioration characteristics of the four different mortars were analyzed using X-ray diffraction, thermogravimetric analysis and optical microscopy. The formed biofilm was characterized by measuring the protein concentration at the sample surface and bacterial respiration. After wastewater exposure, the protein concentration on the Portland cement samples was 50% higher as compared to the geopolymer mortars, while the respiration rates on the Portland/calcium aluminate cement samples was 2.5 times higher than on the geopolymer doped with copper, suggesting a lower bioreceptivity for the latter material. Scanning electron microscopy revealed the presence of biofilm on mortar surfaces, especially on the samples exposed to organic-rich wastewaters. After being exposed to wastewater, the degree of degradation of the geopolymer-based mortars was much lower than the two controls. This may suggest that these materials can be a potential alternative to conventional cement-based binders in order to limit the growth of microorganism on concrete surfaces as well as exhibiting an enhanced acid resistance.

1. Introduction

Biofilm formation and its interaction with concrete surfaces often results in severe deterioration mechanisms while harming structures like sewer piping systems and wastewater treatment plants (WWTP) (Stanaszek-Tomal and Fiertak, 2016; Gutiérrez-Padilla et al., 2010; O'Connell et al., 2010). It is, therefore, that biofilm-concrete interactions are being increasingly investigated because of their high economic impact at a worldwide scale. Annual rehabilitation costs were estimated to reach values of € 456 million in Germany (Berger et al., 2016) and $ 20 billion in USA (O'Connell et al., 2010). Approximately 40% of concrete failure in sewer systems can be directly attributed to microbial induced concrete degradation (MICD) (Berger et al., 2016), where concrete corrosion rates of up to 10 mm/year were observed. It may reduce the repair free service-life of sewer infrastructure due to increased aggressive conditions from 100 years in the past, down to less than 10 years in severe cases (Grengg et al., 2018, 2015). Nevertheless, a clear understanding of the driving interaction mechanism is still lacking. At the inner concrete sewer surface, various complex microbiological processes often induce the chemical deterioration mechanism. Understanding the nature of the phenomena that dominate these processes still requires further knowledge (Lavigne et al., 2015; Grengg et al., 2015). Particularly, information on the initiation of biofilm formation and the biofilm-surface interaction in literature is rare. The porous nature of concrete surfaces enables the growth of harmful microorganisms, which may release/produce corrosive chemicals throughout their active metabolism. Initially, the high alkalinity of concrete pH > 13 provides an antimicrobial environment. However, with time, its abiotic interaction with surrounding chemical species, such as CO_2, acids, or running water, may reduce the surface alkalinity, which makes it more susceptible to microbial growth. In cementitious sewers, where anaerobic conditions are prevalent, the chemical oxidation of hydrogen sulfide (H_2S) produce sulfur compounds with various degrees of oxidation (thiosulfate, tetrathionate, sulfur, sulfate etc.)

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(Okabe et al., 2007; Islander et al., 1991). They are successively metabolized by different bacteria (e.g. sulfur oxidizing bacteria), with sulphuric acid (H_2SO_4) being the final product (Wells and Melchers, 2014; Bielefeldt et al., 2010; Roberts et al., 2002). However, H_2S is also present in the primary clarifiers of municipal wastewater (with very low oxygen concentrations), where it is released from the surface of the water, is entering the local atmosphere, and is oxidized by bacteria at the surface of WWTP components, producing sulphuric acid with a corrosive impact (Stanaszek-Tomal and Fiertak, 2016; O'Connell et al., 2010). Degradation of primary influent channels was reported to be most severe above the waterline (O'Connell et al., 2010). However, so far, no research was done on biofilm formation and biofilm-concrete surface interaction in primarily clarifier wastewaters. Besides this, secondary clarifiers and activated sludge tanks are aerobic environments that are typically not subject to H_2S corrosion. They are affected by various chemical reactions (e.g. oxidation of ammonium to nitrate), which provide acidic environments (production of protons) at the interface between the nitrifying biofilm and concrete surfaces, leading to the dissolution of hydration products, such is $Ca(OH)_2$, and thus continuing the erosion process (Leemann et al., 2010a, 2010b). This whole phenomenon described above is known as “microbiologically induced concrete degradation” (MICD), in which microorganisms cause both initiation, as well as acceleration, of concrete corrosion, due to a sustained acidic environmental exposure.

Furthermore, there is a clear need for research on the behavior of next generation materials with an enhanced durability performance, where geopolymers (GPs) are considered to be among most promising ones (Provis et al., 2015). GPs are produced through alkali activation of metakaolin and volcanic ashes or industrial aluminosilicate waste/by-product materials such as coal ash, biomass ashes, blast furnace slags, red muds or silica fume, individually or together (Duxson et al., 2007a). Alkali activators are potassium or natrium based silicates and hydroxides, generally in liquid form. Many studies have shown that GPs have several advantages over traditional cements, such as a lower CO_2 emission during production (Duxson et al., 2007a), a higher resistance against chemical attack (Bakharev, 2005; Palomo et al., 1999), an increased thermal resistance (Duxson et al., 2006), and a higher versatility, having controlled properties for various applications (Duxson et al., 2007b). Recent studies also proposed the addition of various novel materials (e.g. waste glass, fibres, fly ash selection based on reactivity index approach, Portland cement admixture for hybrid binders) in the process of GP production, in order to achieve a superior mechanical properties of the final product (Liew at al., 2017; Assi et al., 2016; Zhang et al., 2016). Most of the studies done so far focused on the properties of GPs themselves, but effort was also made in developing reliable computer models that are able to predict the alkali leaching behavior (Ukrainczyk et al., 2016).

Field tests of GPs are required alongside standardization procedures to encourage generating long-term data needed to assess their large-scale application potential (Torkaman et al., 2014). Therefore, the next step is to focus on the interactions between GPs and biotic components (mainly bacteria in the form of biofilm), and thereby emphasizing the biochemical behavior of the biofilm on the materials surface. Understanding how microorganisms may interact with the structure of new materials is important as it represents a vital step for estimating the material longevity and for validating their economic performance. Antimicrobial properties of concrete, which have previously been suggested (Hashimoto et al., 2015), need to be verified for GPs as well, but currently the antimicrobial test for concrete is based on the standard ISO 22196 for Plastic materials. A drawback of this adapted test is on the difficulty of letting the specific microorganisms (and associated microbial corrosion) grow, which may take a lot of time and/or requires special environmental conditions, such as H_2S and/or continuously flowing water (Lavigne et al., 2015). Therefore, a reliable way for testing the antimicrobial properties of concrete is needed, and the method proposed in this study, consisting in measuring the protein concentration and bacterial respiration on copper-doped samples exposed to field conditions represents a novel and more realistic approach in this field. In addition, the durability of GPs when facing MICD, together with the nature of GP-biofilm interactions, should be evaluated. The ability of GPs to be used as a protection layer for WWTP/sewer infrastructure, similarly to currently used epoxy systems, or calcium aluminate based products should be analyzed. With the research addressed in this paper, these issues were tackled, as they represent the vital steps in qualifying GPs as a possible substitute for classical cementitious materials.

The main objective of this study was, therefore, to comparatively test the biofilm formation potential (the first step in MICD) of innovative GP-based materials against conventional cement-based solutions, as well as the biofilm-material interactions when exposed to microbes in wastewaters. The potential of GPs to be used in applications like: WWTP/sewage infrastructure, repair mortars and building floors, which are prone to MICD, will be discussed. Two different GPs were investigated: with and without copper additions, as an innovative way to enhance the antimicrobial resistance (Hashimoto et al., 2015). Our results suggest that the bacterial respiration method that was adapted for this study represents a fast and reliable way of estimating the biofilm coverage on environmentally-exposed samples. Furthermore, the findings of this research clarify the relevance of using novel next generation of binders with an improved resistance against biofilm formation and corrosion and show the reliability of these alternative materials to be used in concrete infrastructure.

2. Materials and methods

2.1. Mortars preparation

Four materials were tested: two newly designed geopolymer mortars (GP and GP_Cu) and two conventional mortars based on ordinary Portland cement (PC) and calcium aluminate cement (CAC). CAC is often used as a more expensive conventional solution having a better performance against acid resistance and presumably a lower biofilm affinity. GP_Cu refers to reference GPs, which was doped with copper, in order to test the antimicrobial effect of Cu^{2+} on biofilm formation [2]. The GP_Cu samples are produced by mixing the GP samples with a copper sulphate solution prepared from reagent grade $CuSO_4 \cdot 5\ H_2O$ (purity ≥98%). Chemical composition of the raw materials is given in Table 1. K-waterglass had a solid content of 44%, viscosity of 20 mPa s^{-1}, pH of 13.5, and SiO_2/K_2O molar ratio of 1.5. The cement produced by Holcim is a Portland cement CEM I 52.5 R-SR3/NA. Calcium aluminate cement ISTRA 50 (Calucem) was used, having $CaAl_2O_4$ as main clinker phase and following minor phases $(CaO)_2(Al_2O_3)$

Table 1
Chemical composition (mass %) of the raw materials.

Material	SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	H_2O
PC (CEM I)	21.4	3.7	64.6	4.6	0.8	0.3	0.4	1.5	–
CAC	> 6	50	40	< 2.5	< 1.5	–	–	< 0.4	–
Metakaolin	55	41	< 0.1	< 1.4	< 0.1	< 0.05	< 0.4	< 0.05	–
Waterglass	22						23		55