



Impact of cement composition on the adsorption of hydrogen sulphide and its subsequent oxidation onto cementitious material surfaces



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HIGHLIGHTS

- Adsorption kinetic of H₂S depends on cementitious material types.
- H₂S oxidation leads to elemental sulphur formation followed by gypsum precipitation.
- The mortar composition have only an impact on oxidation kinetic of H₂S.
- After 6 months of H₂S exposure, gypsum severely slows down H₂S adsorption kinetic.
- Abiotic step is not the limiting stage of the whole biodeterioration mechanisms.

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ABSTRACT

Mortars based on different compositions (cast with calcium aluminate cement (CAC), ordinary Portland cement (CEM I), blended Portland cement (CEM III, CEM IV, CEM V) and super sulphated cement (SSC)) were exposed to gaseous H₂S. The most soluble phases from cement lead to the presence of ions in a water layer formed on the mortar surface and these ions provoke acceleration or slowdown of H₂S adsorption. After that, H₂S oxidizes into elemental sulphur and then into gypsum crystals. The cement types only affect the kinetics of these oxidation reactions.

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1. Introduction

Concrete biodeterioration mechanisms in sewerage systems are mainly due to the presence of hydrogen sulphide in the sewer headspace [1]. This gas leads first to a decrease in pH on the concrete surface [2] which allows the enhanced development of sulphur-oxidizing bacteria and the subsequent production of sulphuric acid [1,3,4]. Finally, deterioration of concrete based on dissolution-precipitation mechanisms and on the formation of ettringite and gypsum [5,6] modifies the mechanical properties of the structure and prevents optimum wastewater collection [7,8]. Details of these biodeterioration mechanisms can be found in numerous published studies [9,10] and may be summarized as three successive steps including abiotic reaction of hydrogen sulphide with cementitious materials, biogenic sulphuric acid produc-

tion by sulphur-oxidizing bacteria and structural damage to sewer networks [11]. Due to expensive rehabilitation works, innovative sewerage network construction or repair approaches must be established and evaluated, but few recommendations are available on the choice of materials according to H₂S concentrations. For example in Europe, the German DIN 19573 [12] standard and the French FD P 18–011 [13] standard propose values of H₂S concentration levels to define exposure classes related to aggressive chemical environments (European Standard EN 206/CN: 2014 [14]), but do not provide information on suitable materials for these exposure classes.

Among the many factors affecting concrete biodeterioration rates, more knowledge is needed on the impact of cementitious material types and in particular on the type of cement used. This impact should be determined for the three steps of the biodeterioration mechanisms.

The most commonly used concretes have a surface pH of between 11 and 13 after the cement hydration period. This high

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pH prevents bacteria from colonizing the concrete surface. Rigdon and Beardsley [15] determined that surface colonization by bacteria is possible from a surface pH of concrete equal to 9. The first abiotic step is then essential for studying biodeterioration mechanisms because it establishes an appropriate environment for microorganism development and biofilm formation. It is considered as a latency period before active corrosion of the cementitious materials [16] starts. To date, different authors have conducted abiotic tests and studied the impact of several parameters (temperature, relative humidity, state of deterioration of materials and hydrogen sulphide concentration) on hydrogen sulphide adsorption on cementitious materials based on ordinary Portland cement (OPC) [2,17,18]. Joseph et al. [2] showed that the higher the H₂S concentration, relative humidity and temperature, the higher the H₂S adsorption velocity. Sun et al. [18] conducted some laboratory tests for which mortars based on OPC were exposed to H₂S in abiotic conditions and they showed that pre-exposure to H₂S slows down the H₂S adsorption velocity. They also specified that H₂S adsorption velocity and content could be used to predict the service life of the cementitious material exposed to sewer conditions.

Abiotic oxidation of H₂S has also been studied by some authors [2,9,19,20]. Joseph et al. [2] showed that H₂S oxidation into elemental sulphur takes place in a first step, followed by oxidation of the elemental sulphur into sulphuric acid and gypsum formation. But oxidation of H₂S into ionic sulphur species was not taken into account in the study and the authors considered that elemental sulphur is the main compound formed (90%). Herisson et al. [9] confirmed the presence of elemental sulphur with Scanning Electron Microscopy observations and showed that elemental sulphur formation is better promoted on OPC based mortars than on mortars based on calcium aluminate cement (CAC). Jensen et al. [19] showed that the deterioration products catalyse abiotic H₂S oxidation and that the process is assumed to depend on the amount of these products. According to these authors, H₂S oxidation is mainly due to biotic oxidation reactions rather than abiotic oxidation reactions.

It is important to have more data about interactions of H₂S with different cementitious materials and about deterioration behaviour of these materials in order to better define accelerated tests for comparing material behaviour and also to better predict the durability of materials in sewer systems.

This paper reports on the influence of cement composition, H₂S concentration and relative humidity on the interaction of H₂S with cementitious materials. This study is part of a French project (FUI Duranet) on the improvement of cementitious materials in sewer networks.

2. Materials and methods

2.1. Materials

Mortars were prepared using six types of cement (CEM I, CEM III/B, CEM IV/B, CEM V/A, SSC and CAC), with a siliceous sand to cement ratio of 2.35 and a water to cement ratio of 0.4. The chemical compositions [21] of the different cements are presented in Table 1. CEM I cement is ordinary Portland cement and CEM III, CEM IV and CEM V cements are blended Portland cements with blast furnace slag, pozzolan and a combination between blast furnace slag and fly ash respectively. Calcium aluminate cement and super sulphated cement are also used for this study. Calcium aluminate cement is the hydraulic binder obtained from fusion of a mix of alumina, lime, iron oxide and silica and super-sulphated cement is a cement composed of blast furnace slag (>80%), gypsum (<20%) and clinker (<5%) as an activation compound for blast furnace slag reactivity. The choice of these cements is based on the French FD P 18-011 [13] standard that defines which cements can be used under strongly acidic environmental conditions (but not specifically due to biogenic sulphuric acid as mentioned previously).

After casting, the mortar samples (20 × 20 × 160 mm) were exposed to relative humidity of 100% for 24 h and were then unmoulded and stored in sealed plastic bags for 28 days. After this autogenous curing period, the mortar samples were exposed to the open air for two months. The samples were then sliced into thin sections (20 × 20 × 2 mm) for the study.

2.2. Adsorption test

For each type of mortar, twelve 20 × 20 × 2 mm slices were exposed to gaseous hydrogen sulphide in a hermetic chamber (made of glass with a volume of 8 L). Hydrogen sulphide was produced from the reaction between hydrochloric acid and sodium sulphide. 600 μL of a sodium sulphide solution (20 g.L⁻¹) was injected into a hydrochloric acid solution (0.7 mol.L⁻¹) under agitation to facilitate gaseous hydrogen sulphide emission in the chamber. This injection was realized only once at the beginning of each test. The temperature of the chamber was maintained at 30 ± 2 °C. A sensor (Odalog) with a range between 0 and 200 ppm continuously measured and recorded the hydrogen sulphide concentration and temperature over time. Each test was conducted twice in order to ensure that the results could be reproduced. The two values obtained are presented in the results section and the curves are plotted from the mean values between the two tests. From the decreases in hydrogen sulphide concentration over time, the H₂S adsorption rate was calculated as a function of hydrogen sulphide concentration according to Eq. (1) [18].

$$r_{H_2S} = -\frac{d[H_2S]}{dt} \cdot P_{atm} \cdot \frac{M_{H_2S}}{RT} \cdot \frac{V}{S} \quad (1)$$

where r_{H_2S} is the adsorption rate of H₂S in mg.m⁻².h⁻¹ (in mg of H₂S), $-\frac{d[H_2S]}{dt}$ is the rate of decrease in hydrogen sulphide concentration in ppm.h⁻¹, T is the temperature ($T = 303$ K), R is the gas constant ($R = 8.32 \text{ J} \times \text{K}^{-1} \times \text{mol}^{-1}$), M_{H_2S} is the molar weight of H₂S ($M_{H_2S} = 34 \text{ g} \times \text{mol}^{-1}$), P_{atm} is the atmospheric pressure ($P_{atm} = 101.325 \text{ kPa}$), V is the chamber volume ($V = 8.10^{-3} \text{ m}^3$) and S is the apparent surface of mortars ($12 \text{ slices of } 2 \times 2 \text{ cm}^2, S = 96.10^{-4} \text{ m}^2$).

The H₂S adsorption rate with an empty chamber was systematically subtracted from the rate obtained with cementitious materials in order to only study the H₂S adsorbed by mortars. The empty chamber test was also conducted twice under the same conditions as those with mortars.

Table 1

Composition of the six studied cements (wt%) [21]

	CEM I	CEM III	CEM IV	CEM V	CAC	SSC
CaO	65.67	49.1	33.48	46.36	37.93	39.21
SiO ₂	19.97	29.1	11.18	30.03	5.08	28.77
Al ₂ O ₃	5.51	8.8	3.21	11.15	52.13	10.47
Fe ₂ O ₃	2.77	1.1	2.18	3.59	1.63	0.55
SO ₃	3.97	3.4	2.47	2.80	0.04	5.98
MgO	1.16	4.9	0.53	2.75	0.31	7.11
TiO ₂	0.25	0.6	0.13	0.58	2.06	0.68
K ₂ O	0.25	0.7	0.41	1.16	0.36	0.41
Na ₂ O	0.12	0.18	0.06	0.22	0.08	0.32
P ₂ O ₅	0.38	0.1	0.05	0.61	0.11	0.01
MnO ₅	0.14	0.3	0.05	0.12	0.01	0.34
Cr ₂ O ₃	0.03				0.06	
Cl	-	0.02	0.00	-	-	0.04
Sulphur	-	0.66	0.04	-	-	1.05
Insoluble residue	-	0.4	43.28	-	-	2.94
Loss on ignition	-	0.9	2.78	2.05	-	2.78
Total	100.22	100.26	99.84	101.42	99.80	100.66

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