Performance indicator for cementitious materials exposed to sewer conditions

Amr Aboulela [1,2,3]

[1] *LMDC, Université de Toulouse, UPS, INSA, 31077 Toulouse, France*

[2] *TBI, Université de Toulouse, CNRS, INRAE, INSA, 31077 Toulouse, France*

[3] *Holcim Innovation Center, Saint Quentin Fallavier, France*

RESUME

La biodétérioration des matériaux cimentaires dans les réseaux d'assainissement est principalement due à l'oxydation biologique de H_2S en H_2SO_4 conduisant à une dissolution progressive de la matrice cimentaire ainsi qu'à la précipitation de produits expansifs susceptibles de provoquer des fissurations. Les normes destinées à l'évaluation de ces matériaux en milieu d'assainissement recommandent des essais chimiques par immersion dans une solution d'acide sulfurique (H_2SO_4). Cependant, la comparaison des résultats des tests in situ et chimiques réalisés au laboratoire a montré un classement de performance différent des matériaux. Ainsi, l'objectif de cette étude est de développer un indicateur de performance pour les matériaux cimentaires exposées à un test biologique accéléré (BAC test), utilisé pour reproduire les détériorations observées dans les réseaux d'assainissement.

Différents matériaux cimentaires à base de ciment Portland, de ciment alumineux, de clinker sulfoalumineux et de laitier alcali-activé ont été exposés au test accéléré et l'indicateur de performance (PIeqOH) a été développé par l'évaluation de la lixiviation des éléments/composés chimiques (notamment Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+} et SO_4^{2-}). La meilleure performance a été attribuée au ciment alumineux, suivi par le clinker sulfoalumineux, les ciments à base de Portland et finalement le laitier alcali-activé.

Mots-clefs biodétérioration; acide sulfurique; durabilité; matériaux cimentaires; microorganismes; réseaux d'assainissement.

I. INTRODUCTION

Cementitious materials are widely used in the construction of sewer pipes. Many deteriorations in such environments are associated to the presence of acidophilic bacteria producing sulfuric acid on the surface of the materials (Islander et al., 1992; Parker, 1947). The deterioration process of cement-based materials in sewer networks generally takes place over several months or even years, depending on the environmental conditions (H_2S concentrations, flow rate, temperature, etc.). The need to evaluate the performance of materials in reasonable time of experiments (accelerated test) has led to the use of the Biogenic Acid Concrete (BAC) test. The performance and classification of materials (CEM I, CEM III and CAC) were obtained in previous campaigns and were in accordance with the results obtained in field conditions (Aboulela et al., 2021; Peyre Lavigne et al., 2016).

In this work, cement pastes were exposed to very favorable conditions, using the BAC test, for the development of microbial activity. Acidophilic microorganisms colonize the surface of the material and produce high amounts of sulfuric acid which causes a progressive local dissolution of the cementitious matrix and the formation of secondary expansive phases, e.g. gypsum and ettringite (Alexander and Fourie, 2011; Islander et al., 1992; Okabe et al., 2007; Parker, 1951).

The actual performance criterion used in the BAC test (Aboulela et al., 2021) was based on the calcium leaching from the cementitious matrix. However, this criterion was not optimized for materials containing high amounts of other elements, i.e., alumina, iron, magnesium or sulfur. Hence, works have been done for defining a performance indicator, based on chemical analyses of the leached solutions, capable of capturing with the best efficiency the general deterioration of the materials. The new criterion, called performance indicator equivalent OH^- (PIeqOH), was based on the total amounts of OH^- likely to be released in the leached solutions following the deterioration of the cementitious matrices.

This paper presents briefly the concept of the new performance indicator and the results obtained from different types of binders (Portland cement, calcium aluminate cement, calcium sulfoaluminate clinker and alkali-activated slag).

II. MATERIALS AND METHODS

A. BAC test experimental setup and testing procedures

The BAC-test, for Biogenic Acid Concrete was developed at INSA Toulouse to assess the resistance of cementitious based materials to biogenic acid attack. Cementitious samples are first inoculated with a consortium (an activated sludge) and are then exposed to the trickling of a feeding solution containing a reduced sulfur source, tetrathionate ($S_4O_6^{2-}$), and nutrients. In presence of oxygen, sulfur-oxidizing bacteria in the consortium oxidize tetrathionate ($S_4O_6^{2-}$) into sulfuric acid on the surface of the exposed cementitious samples.

FIGURE 1 shows the BAC-test experimental pilot design (Aboulela et al., 2021; Buvignier et al., 2019). The test pilot consisted of a feeding solution in a 100-liter thermostatic (4°C) tank (1), connected to the specimens by plastic tubes (PTFE natural tube 0.5-1.0 mm) that transported the solution from the tank via flow pumps (regulated at 20 ±5 mL/h) (2) and dropped it onto the top of the specimens (3). The specimens were placed on supports set at an angle of 5° to the horizontal in order to optimize the flow of the solution over the surface of the specimens.

The duration of exposure of the samples to the trickling solution is 3 months. The trickling solution is collected weekly downstream of each sample, and filtered immediately at 0.2 μm, to analyze the concentration of various cementitious cations (calcium, aluminum, iron, magnesium) and to measure the pH.

The optimization of the durability test and the acquired experience and knowledge about the relative performances of a wide range of conventional materials has been published in (Aboulela et al., 2021).

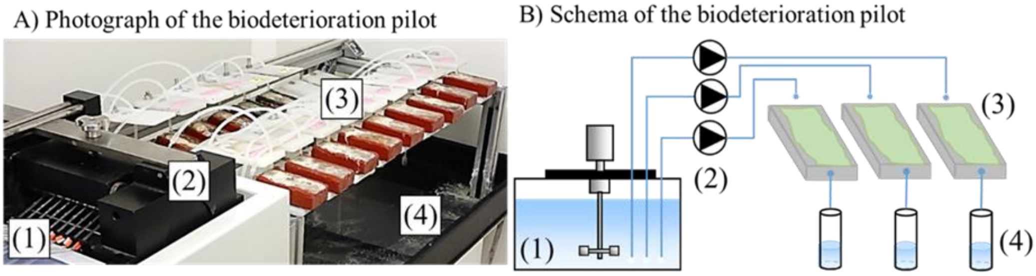

FIGURE 1. A) BAC test pilot; B) Schematic diagram of the BAC test (Aboulela et al., 2021)

B. Cementitious materials

In this work, cement paste specimens, with the size of 8 cm × 4 cm × 2 cm (Length × Width × Thickness), were prepared and cured at 20 °C and 85% of RH for 28 days before the exposure to the BAC test. TABLE 1 present the chemical compositions of the binders used in this study. Six binders were considered for testing their resistance against biodeterioration:

- Reference materials: Portland cement (PC) and calcium aluminate cement (CAC).
- PC-based materials: sulfate-resistant Portland cements (SR0 and SR3).
- CSA-based materials: calcium sulfoaluminate clinker (CSAC).
- AAS-based materials: alkali-activated slag binder (AAS).

TABLE 1. Chemical composition of the studied binders (in weight %)

		CAC	PC	SR0	SR3	CSAC	AAS
Oxides (wt.%)	SiO_2	5.37	20.00	21.30	20.47	7.86	34.68
	CaO	38.10	66.20	64.95	65.05	42.69	41.54
	Al_2O_3	51.20	4.85	3.62	3.57	29.26	9.83
	Fe_2O_3	1.88	2.64	5.80	4.88	11.31	0.28
	MgO	0.52	1.06	0.82	0.73	0.61	6.09
	SO_3	0.02	3.01	1.69	2.79	5.86	0.60

C. Chemical analyses of the leaching solutions

1. pH measurements

The pH was measured with a pH meter directly after collecting the leached solutions at the downstream of the specimens with a precision of 0.01 pH unit for each sample. The solutions were then filtered to 0.2 µm to eliminate all parts of biofilm, microorganisms and particles that could have fallen into the tubes during the collection period. The liquid samples were stored at 4°C to avoid proliferation.

2. Cementitious cations (Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+})

The concentrations of the cementitious cations (Ca^{2+}, Al^{3+}, Fe^{3+}, Mg^{2+}) in the leached solutions were determined using Inductively Coupled Plasma with Optical Emission Spectrometry (ICP-OES). The used ICP-OES equipment was an Optima 7000 DV, with a Meinhart nebulizer. The generator power was 1450 W. The flows of argon and air (auxiliary gas) were 15 L/min and 0.2 L/min, respectively. The flow at the entry of the nebulizer was 0.6 L/min. Finally, the obtained results were processed using treatment and acquisition software (WinLab32).

3. Sulfate (SO_4^{2-}) quantification

The concentrations of sulfate in the leached solutions were measured using High-Performance Ionic Chromatograph (HPIC) (Dionex ICS-3000). In our conditions, because of the microbial sulfur-oxidizing activity in the biofilm on the surface of the materials, the leached solutions contained different types of polythionates, which disturbed the identification and the quantification by usual techniques of the amount of produced sulfate. A dedicated method was thus developed to measure the sulfate concentrations after separating the sulfate from the other polythionates. In particular, the pre-column and column were a Dionex AG11 and an IonPac AS11-HC, respectively. The column flow was of 1.5 ml/min. The gradient of eluent (KOH) was between 1 and 60 mM, and the column temperature was of 30°C. A suppression system (AERS 500 4 mm) was used to increase the sensitiveness and to reduce the background conductivity of the eluent.

III. RESULTS AND DISCUSSION

A. Bacterial activity and sulfate production

The pH of the leached solutions and the concentration of sulfate were measured at the outlet of the specimens to monitor the biogenic acid production linked to the microbial activity. FIGURE 2 presents the evolution of the pH and the cumulative measured sulfate for cement pastes during the exposure period to the BAC test.

At the early days of the testing period, the pH of the leached solutions for all materials was relatively high (around 11 for Portland-based materials (SR0 and SR3) and alkali-activated slag (AAS) and around 10 for calcium aluminate (CAC) and calcium sulfoaluminate (CSAC) materials).

During the first 3 weeks of the exposure period, the development of neutrophilic sulfur oxidizing bacteria (NSOB) was being carried out naturally due to the favorable conditions for their development. However, the activity of NSOB was limited by the high pH and therefore, the amount of produced sulfate was very low. Materials CAC, CSAC and AAS showed faster acidification compared to PC-based materials (PC, SR0 and SR3). Following these 3 weeks, a period of transition was identified and linked to the progressive development of acidophilic sulfur-oxidizing bacteria (ASOB), accompanied with an increase in sulfate production (Islander et al., 1992; Okabe et al., 2007). The sudden increase in pH for AAS at 35 days was due to a problem with the pump of the feeding solution, resulted in drying the specimen for 24 hours. Finally, when the pH was below 4, the sulfate production increased significantly for all materials; however, no significant difference was observed between the different materials.

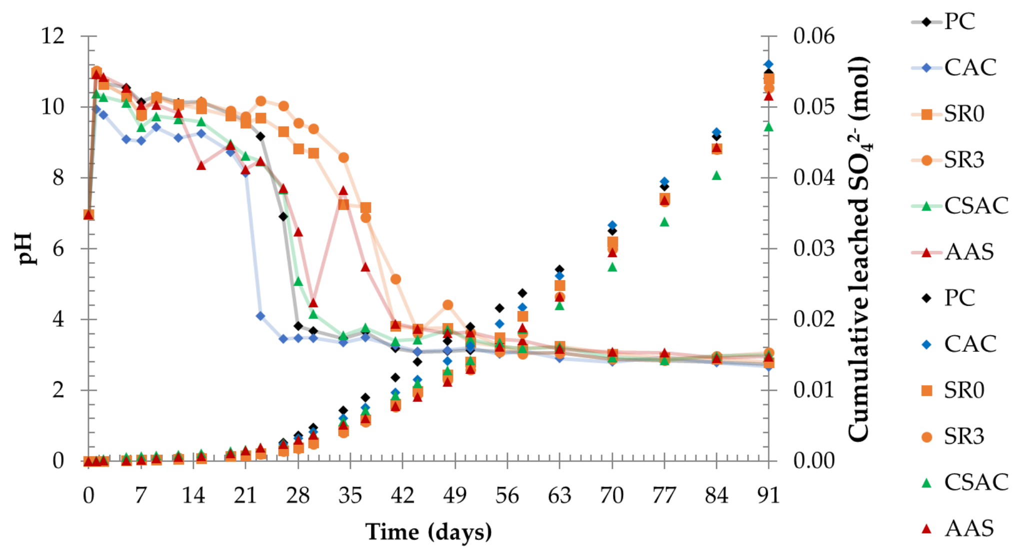

FIGURE 2. Evolution of the pH (solid lines) and the measured cumulative measured SO_4^{2-} (dots) in the leached solutions of the different materials during the 3-months exposure period to the BAC test

B. Development of the performance indicator approach

The parameter "equivalent OH" (eqOH) was developed to consider the impact of the different chemical elements (as well as the mineralogical phases) on the resistance of materials based on the five major ions susceptible to be leached from the cement matrix, calcium, aluminum, iron, magnesium and sulfur.

The equivalent OH represents the total amount of OH^- to be released from the dissolution of the main oxides in a cementitious matrix (CaO, Al_2O_3, Fe_2O_3, MgO and SO_3). TABLE 2 presents the dissolution reactions which were considered for the total dissolution of cementitious oxides and the corresponding eqOH per mole of ion released from the cement matrix.

TABLE 2. Respective dissolution reaction considered for the main oxides of a cement-based material

Oxide	Dissolution reaction	eqOH (in moles) for 1 mole of the corresponding ions	
CaO	$CaO + H_2O \rightarrow Ca^{2+} + 2\ OH^-$	2	**Eq. 1**
Al_2O_3	$Al_2O_3 + 3\ H_2O \rightarrow 2\ Al^{3+} + 6\ OH^-$	3	**Eq. 2**
Fe_2O_3	$Fe_2O_3 + 3\ H_2O \rightarrow 2\ Fe^{3+} + 6\ OH^-$	3	**Eq. 3**
MgO	$MgO + H_2O \rightarrow Mg^{2+} + 2\ OH^-$	2	**Eq. 4**
SO_3	$SO_3 + 2\ OH^- \rightarrow SO_4^{2-} + H_2O$	-2	**Eq. 5**

The total dissolution of SO_3 (reaction Eq. 5) was reported to consume 2 moles of hydroxide based on the mass balance calculations. Furthermore, silicon was not considered in the calculations of the equivalent OH as the silica dissolution is considered very low in the conditions of the BAC test. The calculations for the eqOH were similar to that of the **standardization of the leached calcium per initial total calcium in the materials per exposed surface**, presented in (Aboulela et al., 2021) . The same calculations for the calcium were carried out for aluminum, iron, magnesium and sulfate in order to obtain the standardized cumulative leached amount of these ions.

The approach of using the equivalent OH enabled to consider the hydrated and anhydrous phases of the material, since both forms of phases are dissolved during biologic sulfuric acid attack on cementitious materials. Finally, the development of the PIeqOH was based on the calculations from the eqOH and it is expressed for a material "X" in Eq. 6, with $eqOH_{PC}$ corresponding to the value for PC:

$$PIeqOH_{x} = 100 \text{ x } (eqOH_{PC} / eqOH_{x}) \quad \text{,expressed in \%} \qquad \textbf{Eq. 6}$$

C. Performance of cement-based materials exposed to biodeterioration in sewer-like environment

FIGURE 3 presents the classification of materials according to their PIeqOH as a function of the cumulative estimated biogenic acid (The acid calculations were obtained through a developed model based on the sulfur cycle in the system and are not presented in this paper). The control material (PC) had a PI of 100%, which means that materials with PIeqOH above 100% performed better than the PC and materials with PIeqOH lower than 100% did not perform as well as the PC.

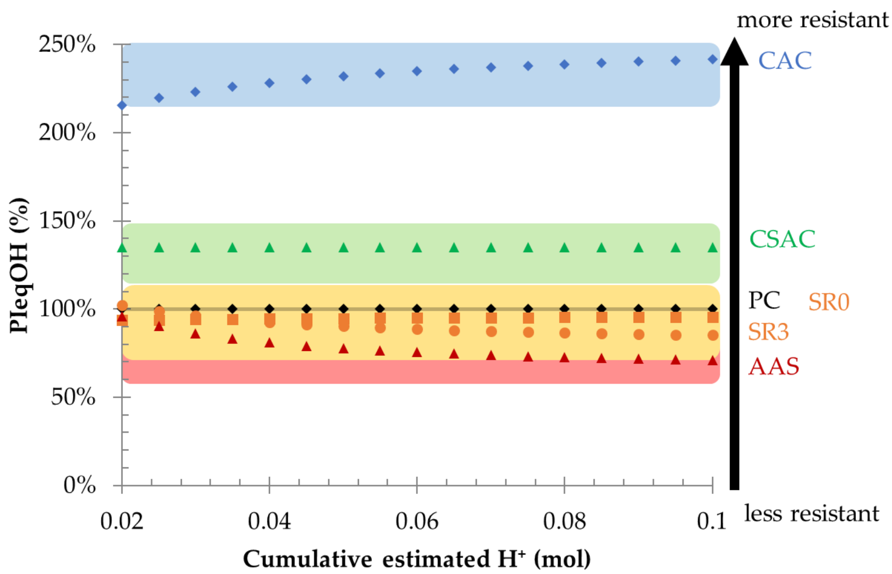

FIGURE 3. The performance indicator eqOH (PIeqOH) of the different binders as function of the cumulative estimated acid in the leached solution

Firstly, CAC material showed very good performance with an average PIeqOH of 233%, which was slightly more than double of the reference cement. This result was in accordance with the literature indicating the very good resistance of calcium aluminate cement to biogenic sulfuric acid attack (Buvignier et al., 2019; Herisson et al., 2017; Lamberet et al., 2008; Letourneux and Scrivener, 1999).

Secondly, SR0 and SR3 had average PIeqOH of 95 and 85% respectively. While sulfate resistant cements (SR) are used mainly when the material is exposed to high sulfate environments due to their lower C_3A content, the results showed no significant impact of decreasing C_3A amount and increasing C_4AF amount on the performance of the PC materials in sewer conditions. Overall, PC-based materials showed very similar performances, indicating that mainly calcium-bearing hydrated phases were responsible for the chemical resistance of these materials.

Thirdly, CSAC showed a better overall performance compared to Portland cement. The average PIeqOH was 135%. The performance of CSA was not as good as that of CAC but was still an increase up to 30% in the resistance of the binders compared to PC. The slightly higher resistance of calcium sulfoaluminate material, compared to PC, could be linked to the similarity in the initial oxide composition with CAC (Higher alumina and lower lime than Portland cement) which led to form alumina-based phases, known to be more resistant against acid attack (Letourneux and Scrivener, 1999). In addition, CSA matrix have higher resistance to external sulfate attack than Portland cement due to the absence of C_3A, absence or very low amount of portlandite, non-reactivity of ettringite with sulfate and a denser microstructure (Glasser and Zhang, 2001; Guo et al., 2014).

Fourthly, alkali-activated slag (AAS) material performed the poorest in these conditions, with PIeqOH 78% compared to Portland cement. While the use of slag-based alkali-activated binder increased the initial aluminum content, the amount of aluminum was still very low compared to CAC and CSA materials. Moreover, the hydration of alkali-activated slag produces C-A-S-H with a Ca/Si ratio typically around 1.1-1.2 and Al/Ca around 0.19 (Taylor, 1997). These phases are composed of tetrahedron $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, increasing their durability against acid attack compared to hydrated calcium silicates in the Si-O-Al system (Allahverdi and Škvára, 2005, 2001). However, the hydration of this material seemed to not be carried out in optimal conditions (i.e., lack of thermal curing) which resulted in lower performances (results are not presented).

IV. CONCLUSIONS AND PERSPECTIVES

This paper presented the development of an optimized performance indicator based on the analyses of the leached solutions, from different cementitious materials, obtained from an accelerated laboratory test for biodeterioration phenomena over 3 months of exposure.

The performance indicator equivalent hydroxide (PIeqOH) was based on the amount of hydroxide ions potentially released from the dissolution of the corresponding mineralogical phases. The evaluation of OH^- quantity was linked to five major elements/compounds constituting the cement matrix: calcium, aluminum, iron, magnesium and sulfate. By using the amount of acid produced and the PIeqOH, a performance ranking for all materials was obtained.

CAC was found to provide the best performance, with a performance indicator equivalent to 2.3 times the reference material. CSA clinker showed a promising performance with PIeqOH averaging 1.3 times the performance of the PC material. The performances of the PC-based materials were very similar. Finally, the resistance of alkali-activated slag materials was lower than that of Portland cement, indicating a very poor performance of such materials in the sewer conditions.

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