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Modelling of the sulfuric acid attack on different types of cementitious materials

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Abstract

A chemical-reactive transport model was used to simulate the sulfuric acid attack of cement pastes based on ordinary Portland cement (CEM I), blended Portland cements (CEM III, CEM IV, and CEM V), and calcium aluminate cement (CAC). This model accounts for the dissolution of cement hydrates (portlandite, C-S-H, hydrogarnet), and the precipitation of deterioration products (ettringite and gypsum). Moreover, diffusion of the aqueous species in the pore space in the material is considered. With this model, we can get the hydrate contents, the porosity, and the deterioration phase contents throughout a sulfuric acid attack. Two indicators are defined to predict the service life of the cementitious materials: the deterioration depth and the dissolved calcium content. These two indicators showed that calcium aluminate cement provide a better resistance to sulfuric acid attack than that of Portland cements. This better resistance is mainly due to the partial dissolution of CAC hydrate as opposed to the total dissolutions of CH and C-S-H.

Keywords: Deterioration (C.), Calcium Aluminate Cement (D.), Portland cement (D.), Modelling (E.), Acid attack

1. Introduction

Concrete can undergo severe deteriorations in sewer pipe conditions, caused by gaseous hydrogen sulphide (Figure 1) [1, 2]. Concrete gravity sewers are divided into two parts: a liquid part and an aerial part (sewer atmosphere). The liquid part contains waste water which is composed of sulfate ions and sulfate reducing bacteria (SRB). The cementitious wall in the aerial part is covered by a biofilm mainly

28 composed of sulphur-oxidizing bacteria (SOB). Aqueous hydrogen sulfide is produced in the anaerobic
29 zone (waste water stagnation) from the reduction reaction of sulfate ions due to sulfate reducing bacteria.
30 Then, H₂S escapes into the sewer atmosphere, where it is adsorbed onto the cementitious wall [3]. Due
31 to the high relative humidity at the surface of the wall, gaseous hydrogen sulphide dissociates into
32 hydrogen ions and sulfide ions. Hydrogen ions contribute to surface pH neutralization, giving rise to the
33 biofilm development [4]. Under such aerobic conditions, sulfide ions oxidize into several sulphur
34 species, which are used as nutrients for the microorganisms of the biofilm. Sulfuric acid is produced by
35 the oxidation reactions of these sulphur species [5, 6]. This acid attacks the cementitious walls and
36 produces gypsum and ettringite [7, 8], which are expansive and cause severe damage of the sewer
37 system. The sulfuric acid produced by these microorganisms diffuses through the altered layer and
38 continually attacks the underlying concrete [9].

39 Numerical models of acid attack of cementitious materials [10-17] can be found in the literature. One
40 of these models simulating the biochemical process and the sulfide oxidation is named “Wastewater
41 Aerobic/anaerobic Transformations in Sewer” (WATS) [10, 11]. Another study [12] simulates sulfuric
42 acid attack with a diffusion-reaction based model with a moving boundary to predict the corrosion rate.
43 A reactive-transport model (HYTEC [13]; [14]) was also used to simulate the attack of cementitious
44 materials by different types of organic acids. This model takes into account chemical interactions
45 between these different organic acids and hydrates of cementitious materials based on Portland cement.
46 Another model [15] has been proposed to simulate the acid attack of OPC and is based on the HYTEC
47 model [14]. In this model, the dissolution of the main hydrates of the cementitious materials and the
48 precipitation of deterioration products are simulated, using chemical equilibrium associated with
49 thermodynamic constants and the transport of different species during sulfuric acid attack.

50 Some experimental studies [9, 18-21] in the literature have focused only on sulfuric acid attack of
51 cementitious materials. For cementitious materials based on Portland cement, Bassuoni et al. [18]
52 observed the dissolution of portlandite and the decalcification of C-S-H, which are the main hydrates of
53 Portland cement, leading to mass loss. Kawai et al. [19] showed that cementitious materials containing

54 a high amount of silica fume have a better resistance than those containing fly ash or blast furnace slag.
55 Jiang et al. [21] determined deterioration product localizations during these chemical reactions. Gypsum
56 is the first product formed from the reaction between hydrates and sulfuric acid followed by ettringite
57 localized near the undeteriorated concrete. Thermodynamically, ettringite is stable at pH greater than
58 10.7 [22] and forms only for high pH conditions. All these tests were performed on cementitious
59 materials based on Portland cement or blended Portland cements. Several *in-situ* experiments (with
60 microorganism presence) carried out by Alexander and Fourie [8] and Herisson et al. [23] suggested
61 that cementitious materials based on calcium aluminate cement (CAC) have a better resistance than that
62 of ordinary or blended Portland cements. Moreover, several laboratory tests of biodeterioration also
63 showed better resistance for CAC materials [24-27].

64
65 In the present research, the behavior of cementitious materials based on different types of cement in
66 contact with sulfuric acid was simulated with a predictive model based on the model of Yuan et al. [15].
67 The cements were ordinary Portland cement (CEM I), blended Portland cements (CEM III, CEM IV,
68 and CEM V), and calcium aluminate cement (CAC). The aim of this study was to predict deterioration
69 depth of cement subjected to sulfuric acid attack and to determine which one has a better resistance to
70 this kind of corrosion. In this study, the biological acid production, depending on numerous parameters,
71 is not modeled. Instead, it is assumed that, due to a lack of data concerning interaction of microorganisms
72 and cementitious materials and its consequence on acid production, the considered hypothesis is that
73 microorganisms produce sulfuric acid in such a way that sulfuric acid concentration is constant. This
74 model is then static. Despite of this hypothesis, the model results obtained may be compared with those
75 from experimental *in-situ* and laboratory tests for which microorganism activity can be dependent on
76 environmental and material parameters.

77

78 **2. Hydrate composition of cements**

79 The cementitious materials considered were cement pastes with a water to cement ratio of 0.4. The
80 hydrate compositions and contents are presented in Table 1 and expressed in mole per liter of cement

81 paste. Initial data used for the model are porosity and hydrate amounts for each type of cement. For
82 cement pastes based on CEM I, CEM III, CEM IV, and CEM V cements, the main hydrates are calcium
83 silicate hydrate (C-S-H) and portlandite (CH) and for cement pastes based on calcium aluminate cement,
84 the main hydrates are hydrogarnet (C_3AH_6) and gibbsite (AH_3). The chosen porosities are those of
85 mortars, even if in the model, the cementitious materials considered are cement pastes. This
86 consideration allows comparing model results (diffusion-controlled model leading to a high effect of the
87 porosity) and experimental results.

88 Hydrate amounts were experimentally measured by TGA and Rietveld XRD techniques and the
89 porosities were measured by the water absorption method [28]. The portlandite contents for CEM III,
90 CEM IV, and CEM V cements are lower than that for CEM I cement, because the clinker is substituted
91 by other compounds: blast furnace slag for CEM III cement, natural pozzolans for CEM IV cement, and
92 a combination of blast furnace slag and fly ash for CEM V cement. In this model, the other phases of
93 blended Portland cements (hydrates from the additions and anhydrous phases) were not taken into
94 account in the chemical processes and the differences between the Portland cements are only controlled
95 by the portlandite and C-S-H contents and the porosity.

96 With the purpose of comparing the behavior of cement pastes, the same calcium content is considered
97 for all the cement, namely 6 mol/L. The C-S-H content is then deduced from a calcium to silicon ratio
98 equal to 1.7 and the CH content. This assumption which may not reflect the reality, was considered with
99 the aim of giving the same potential of calcium dissolution to all materials. Indeed, it is clear that the
100 more the calcium content the better the resistance to calcium dissolution.

101 For the CAC materials, there are four main hydrates: C_3AH_6 , AH_3 , C_2AH_8 , and CAH_{10} . If CAC paste
102 undergoes heat treatment during the hydration mechanisms, the major hydrate is the stable hydrogarnet
103 (C_3AH_6) but if the hydration mechanisms take place at room temperature, the major hydrates formed are
104 two metastable phases (CAH_{10} and C_2AH_8). AH_3 (gibbsite) is formed in both cases. During heat
105 treatment, the conversion reaction provokes the transformation from metastable hydrate to the stable
106 hydrate. The conversion reactions are partial and begin from a curing temperature of 28°C, reaching a

107 conversion rate of 100% for a temperature of 60°C [29]. For the model, only a CAC paste with C_3AH_6
108 as the main hydrate is considered. Lamberet et al. [30] indicate that the gibbsite (AH_3) is stable for a
109 surface pH of the cementitious material between 4 and 11. The CAC cement paste simulated in this
110 study has a surface pH of 12 in the initial state. Therefore, gibbsite is not present initially. This hydrate
111 can precipitate when the cementitious material is carbonated, inducing a surface pH around 7-8.
112 However, the carbonation is not considered in this study and so the initial content is taken to zero (Table
113 1).

114 **3. Modelling of the H_2SO_4 attack of concrete**

115 **3.1. Chemical reactions and thermodynamic constants**

116 The reactive-transport model presented in Yuan et al. [15] takes into account the dissolution of CH and
117 C-S-H and the precipitation of gypsum, so only the phase diagrams of the systems CaO-SiO₂-H₂O and
118 CaO-SO₃-H₂O were considered. Alkali ions were also included in the system. In the present study, the
119 model was improved by considering the system CaO-Al₂O₃-SO₃-H₂O, in addition to CaO-SiO₂-H₂O.

120 All the dissolution reactions implemented in the new model are listed in Table 2, for the heterogeneous
121 reactions (in solid and aqueous phases) and in Table 3 for the homogeneous reactions (in only aqueous
122 phase). The thermodynamic constant values are obtained from a data base (*CEM DATA 14.01*). This
123 system contains stable and metastable phases. For CAC materials, Damidot et al. [31] determined that
124 the metastable phase AFm crystallizes only when CAH_{10} and C_2AH_8 are formed at 25°C, whereas the
125 stable phase AFt (ettringite) crystallizes only when C_3AH_6 is formed. As a result, in this system, AFm
126 does not precipitate during the simulation.

127 **3.2. Stability of solid phases**

128 The stability of each solid phase can be described by the equality between the equilibrium constant (K)
129 and the ion activity product (Q). The ratio between Q and K defines the saturation index β . If β is lower
130 than unity, the solid phase would not precipitate and if β is greater than unity, the solid phase would
131 precipitate. For each solid phase, a saturation index is defined as a function of β_{CH} , β_{AH_3} , and $\beta_{H_2SO_4}$,

132 according to equations 1 to 6. β_{CH} , β_{AH3} , and a_{H2SO4} are respectively the saturation indexes of portlandite
133 and gibbsite and the activity of H_2SO_4 (taken equal to H_2SO_4 concentration) and they are considered as
134 primary variables. After the Gibbs phase rule, the system $CaO-SO_3-Al_2O_3-H_2O$ has 3 degrees of freedom
135 at the most (at constant pressure and temperature), namely β_{CH} , β_{AH3} , and a_{H2SO4} . The other saturation
136 indexes can be derived from the mass action law under the form:

$$137 \quad \beta_{CSH2} = 10^{31.4} \beta_{CH} a_{H2SO4} \quad (1)$$

$$138 \quad \beta_{C3AH6} = 10^{4.59} \beta_{CH}^3 \beta_{AH3}^2 \quad (2)$$

$$139 \quad \beta_{CAH10} = 10^{-0.22} \beta_{CH} \beta_{AH3}^2 \quad (3)$$

$$140 \quad \beta_{C2AH8} = 10^{67.4} \beta_{CH}^2 \beta_{AH3}^2 \quad (4)$$

$$141 \quad \beta_{AFm} = 10^{38.4} a_{H2SO4} \beta_{CH}^4 \beta_{AH3}^2 \quad (5)$$

$$142 \quad \beta_{AFt} = 10^{107.5} \beta_{CH}^6 \beta_{AH3}^2 a_{H2SO4}^3 \quad (6)$$

143 From equations 1 to 6, the stability zones of each solid phase included in this system are plotted in the
144 phase diagram (Figure 2).

145 The continuous decalcification of C-S-H, during acid attack, is simulated in the present study by a
146 thermodynamic approach presented in [32].

147 **3.3. Kinetic law**

148 Portlandite, AH_3 , and C-S-H are assumed in equilibrium with the solution. Dissolution and precipitation
149 rates for C_3AH_6 , gypsum, ettringite, and AFm are governed by a simple kinetic law (Equation 7).

$$150 \quad \frac{dn_A}{dt} = R_A (\beta_A - 1) \quad (7)$$

151 In Eq. (7), n_A is the amount of solid A in mol/L, R_A is the kinetic factor of the solid A in mol/L/s and β_A
152 is the saturation index of the solid A.

153 The kinetic factors introduced in this law ($R_{C_3AH_6}$, R_{AFt} , R_{AFm} , and R_{gypsum}) are adjusted so that
154 equilibrium is quickly reached. Indeed, this kinetic law is governed by interface reactions. But, interface
155 reactions are quicker than diffusion of aqueous species in the porous system in cementitious materials.
156 As a result, the kinetic factors should be fixed as high as possible value, so as to get a saturation index
157 as close as possible to 1. But, the model does not converge with too big kinetic factors, so some
158 simulation tests are performed by increasing the factors as high as possible. The values chosen are
159 presented in Table 4.

160 **3.4. Porosity change**

161 During the chemical reactions, the change in porosity ($\Delta\phi$) is given by the volume change of the solid
162 phases (ΔV_{solid}) according to equations 8 and 9.

$$163 \quad \Delta\phi = -\Delta V_{\text{solid}} \quad (8)$$

164 Where $V_{\text{solid}} = \sum_i V_i n_i$ with summation over all solids, V_i is the molar volume of each solid phase of
165 the cement paste in L/mol and n_i is the amount of each solid phase in mol/L (CH, C-S-H, C_3AH_6 , AH_3 ,
166 C_2AH_8 , CAH_{10} , $C\bar{S}H_2$, AFm, and AFt).

167 The molar volume of C-S-H (V_{C-S-H}) included in equation 9 is a function of the calcium to silicon ratio,
168 according to [15].

$$169 \quad V_{C-S-H}(x) = (x/x_0)V_{C-S-H}^0 + (1 - x/x_0)V_{SH} \quad (9)$$

170 Where x is the calcium to silicon ratio at a fixed time of sulfuric acid attack, x_0 is the initial calcium to
171 silicon ratio of the cement paste ($C/S = 1.7$), V_{C-S-H}^0 and V_{SH} are the molar volumes of C-S-H at the
172 initial state ($78 \text{ cm}^3/\text{mol}$ for $C_{1.7}SH_{2.1}$) and of silica gel ($29 \text{ cm}^3/\text{mol}$).

173 **3.5. Reactive transport model**

174 The system is controlled by chemical equilibrium but also by the transport of aqueous species. The
175 coupling between these two mechanisms is taken into account within the modelling platform Bil [33],

176 based on the finite volume method. This coupling is treated with a mass balance equation (Equation 10),
177 a global balance equation for the charge (Equation 11), and an equation for the electroneutrality to form
178 an electroneutral pore solution (Equation 12). These equations are detailed in the study of Yuan et al.
179 [15].

$$180 \quad \partial n_A / \partial t = -\text{div } \mathbf{w}_A \quad (10)$$

$$181 \quad \text{div } \underline{i} = 0 \quad (11)$$

$$182 \quad \sum_i z_i \rho_i = 0 \quad (12)$$

183 Where $\underline{i} = \sum_i z_i \mathbf{w}_i$ is the ionic current and n_A is the mole content of element A in all phases per unit
184 volume, \mathbf{w}_A is the molar flow vector of element A in the liquid phase, z_i is the ionic valence of i , \mathbf{w}_i is
185 the molar flow of i , and ρ_i is the concentration of i .

186 The transport of aqueous species is governed by the Nernst-Planck equation, previously detailed in the
187 study of Yuan et al. [15]. According to Bazant-Najjar law [34], the evolution of the effective diffusion
188 coefficient is:

$$189 \quad D_p / D_0 = 2.9 \cdot 10^4 \cdot \exp(9.95 \cdot \phi) \quad (13)$$

190 D_p is the effective diffusion coefficient of aqueous species in the porous materials, D_0 is the effective
191 diffusion coefficient in bulk water and ϕ is the porosity of the system at the current time and defined by
192 the equation 8.

193 **3.6. Description of the simulations**

194 These one dimensional (1D) studies aim at simulating the chemical processes in sewer pipes made of
195 different cement types (CEM I, CEM III, CEM IV, CEM V cements, and CAC). The simulations are
196 conducted in 1D only. The 2 cm long sample is discretized in 200 elements (finite volume). The
197 boundary surface represents the interface between the cementitious materials and the H_2SO_4 solution.
198 The initial H_2SO_4 concentration in the pore solution of samples is set to 10^{-32} mol/L, a very small value

199 consistent with the stability of the cement hydrates. At the boundary surface, the H_2SO_4 concentration
200 is set to 10^{-1} mol/L, in order to study the deteriorations in extreme conditions. The damage model caused
201 by gypsum formation as modeled in [15] was not extended to CAC system because this is ettringite
202 which is mainly formed in CAC. So, in order to compare the durability of cement pastes, the
203 deterioration depth is introduced as the distance between the first point where the porosity exceeds the
204 initial porosity and the boundary surface.

205 **4. Results and Discussion**

206 **4.1. Profiles of the solid content**

207 The initial data for each type of cementitious material are summarized in Tables 1 and 4. All the results
208 are simulated for one year with a H_2SO_4 concentration of 10^{-1} mol/L at the boundary surface of the
209 cement pastes. The calculated profiles of solid phase contents, of the calcium to silicon ratio for the
210 Portland cements and of the porosity, are plotted in Figure 3.

211 **4.1.1. Profiles of the solid contents for ordinary or blended Portland cements**

212 As indicated in Figure 3, the initial amount of portlandite for CEM I, CEM III, CEM IV, and CEM V
213 cements (Table 1), is completely dissolved into calcium and hydroxide ions at a distance of 2-3 mm
214 (depending on cement type) from the boundary surface. The depth which corresponds to this total
215 dissolution, defines the dissolution front of portlandite.

216 The calcium to silicon ratio, drops down to 0 at a depth equivalent to the dissolution front of portlandite
217 and corresponds to the decalcification front of C-S-H. This total decalcification ($\text{C/S} = 0$) infers that C-
218 S-H turns into silica gel near the boundary surface.

219 These two dissolutions induce the presence of calcium ions at the common dissolution and
220 decalcification fronts of portlandite and C-S-H, and these ions react with sulfate ions from sulfuric acid
221 solution and form a gypsum layer. The thickness of the gypsum layer is 2.0 mm for CEM I and CEM V
222 cements and 2.4 mm for CEM III and CEM IV cements. The gypsum content at the surface reaches
223 around 6 mol/L for all the Portland cements. Moreover, ettringite in ordinary or blended Portland

224 cements is considered negligible. The detection of this phase is infrequent in experimental studies [24-
225 26].

226 For the ordinary and blended Portland cements, porosity is equal to the initial porosity of each
227 cementitious material until reaching the corresponding depth to the dissolution and decalcification fronts
228 of portlandite and C-S-H. Indeed, when the two hydrates start to dissolve, new porous space is created
229 and is partially filled by the precipitation of gypsum, leading to a porosity increase near the boundary
230 surface. This porosity increase shows that gypsum does not fill the total porosity and its swelling cannot
231 provoke structural damages.

232 **4.1.2. Profiles of the solid contents for CAC cement**

233 A different behavior is observed for the calcium aluminate cement. The acid attack (Figure 3) leads to
234 a partial dissolution of the hydrogarnet (C_3AH_6). Indeed, the initial hydrogarnet amount is equal to
235 2 mol/L and decreases to 1.75 mol/L, after 1 year of sulfuric acid attack. The hydrogarnet dissolution is
236 slower than portlandite dissolution and C-S-H decalcification observed in Portland cements. Gypsum
237 does not precipitate in this cementitious material, the saturation index being lower than 1 during the
238 simulation whereas the gibbsite and ettringite precipitate. The ettringite precipitation is due to the
239 reaction between calcium ions and aluminum ions from the partial dissolution of the hydrogarnet and
240 sulfate ions from the sulfuric acid solution (the maximum amount reached is $1.8 \cdot 10^{-1}$ mol/L). This
241 precipitation tends to clog up the pores of this cementitious material, with the porosity reaching a value
242 close to zero (10^{-10} %) at the depth corresponding to the maximum amount of ettringite. When the pH
243 of the system drops down below 10.7, ettringite starts to dissolve [22] and causes an increase of porosity
244 which reaches at the boundary surface a value slightly greater than the initial porosity of the CAC (Table
245 1). The gibbsite forms near the boundary surface with a maximum content reaching $1.5 \cdot 10^{-1}$ mol/L. This
246 solid phase fills pores but this precipitation does not compensate the voids created by the dissolution of
247 ettringite (the molar volume of ettringite is $710 \text{ cm}^3/\text{mol}$, whereas that of gibbsite is $64 \text{ cm}^3/\text{mol}$),
248 resulting in an increase of porosity. As shown in the phase diagram (Figure 2), gypsum is not stable in
249 presence of hydrogarnet. This is why simulations don't find any gypsum. However, in some

250 experimental studies [35], gypsum can be found in the near surface zones of CAC binders attacked by
251 sulfuric acid.

252 Damage caused by the ettringite precipitation is not implemented in this study. Experimental studies
253 [20, 21, 36] have shown some degradations that were explained by the important expansion of ettringite
254 precipitation (needle like crystals creating locally micro-cracking). In the present study, ettringite fills
255 the porous space and prevents the sulfuric acid from penetrating into the cementitious material. This
256 phase has then a protective function.

257 **4.2. Determination of the deterioration depth and of weight loss for different cementitious material** 258 **types**

259 The porosity profiles over depth obtained after one year of acid attack are plotted in Figure 4. The
260 deterioration depth reached after one year of acid attack and the evolution of this parameter over time
261 for each cementitious material are respectively proposed in Table 5 and Figure 5.

262 The deterioration depths obtained for CEM I, CEM III, CEM IV, and CEM V cements (Figure 4) are
263 deeper than that obtained for CAC materials. Specifically, the deterioration depth reached after 1 year
264 of acid attack for the CAC material is 10 times lower than that for the ordinary or blended Portland
265 cements (Table 5 and Figure 5). Therefore, the CAC cement paste is clearly the most sustainable cement
266 in acid conditions. The low deterioration kinetic for CAC materials is observed in many experimental
267 field and laboratory studies [8, 20, 23, 26, 27, 39, 40]. In the model, this delaying effect is then due to
268 the better stability of hydrogarnet in acidic conditions than the portlandite and C-S-H and to the ettringite
269 formation, which clogs up the porosity of the material.

270 Several studies showed that an increase of the porosity causes a decrease of the compressive strength
271 [37, 38]. The porosity increases from 11 to 22% for CEM I cement, from 14 to 25% for CEM III cement,
272 from 16 to 26% for CEM IV cement and from 11 to 23% for CEM V cement, whereas the porosity
273 increases from 10 to 13% for the CAC material. The ordinary or blended Portland cements undergo a

274 comparable decrease of compressive strength and a more important decrease than that of CAC,
275 highlighted the better resistance of CAC materials to acid attack.

276 Some differences are observed between Portland cements. The deterioration kinetic is quicker for CEM
277 III and CEM IV cements than for CEM I and CEM V cements (Figure 5). These results are mainly due
278 to the high porosity of CEM III and CEM IV cements as compared to the porosity of CEM I and CEM
279 V cements (Table 1). But, these qualitative important differences between these Portland cements need
280 to be confirmed. Indeed, other hydrates than C-S-H and portlandite for blended Portland cements or
281 anhydrous phases were not taken into account in the model. Specifically, the phases from the hydration
282 of blast furnace slag, natural pozzolans, and fly ashes, leading to C-A-S-H and C-S-H with different C/S
283 ratio and anhydrous phases should be considered.

284 The dissolved calcium contents are determined for each cementitious material after 1 year of sulfuric
285 acid attack and are presented in Table 6. This parameter is plotted over time (Figure 6) and allows
286 characterizing cementitious materials deterioration, with data about the loss of matter during the acid
287 attack.

288 The dissolved calcium content reached after 1 year of sulfuric acid attack for the Portland cements is
289 more than two times greater than the value for the CAC material (Table 6), highlighting the partial
290 dissolution of hydrogarnet and the total dissolutions of CH and C-S-H. The evolution of the dissolved
291 calcium content is linear with \sqrt{t} for CEM I, CEM III, CEM IV, and CEM V cements. For CAC cement,
292 this parameter is almost linear with time. But, this evolution is considered as linear with \sqrt{t} (the
293 correlation coefficient is equal to 0.92), in order to compare the cementitious materials.

294 **4.3. Long-term prediction**

295 The deterioration depths obtained are only calculated over 1 year of sulfuric acid attack. Yuan et al. [15]
296 considered the evolution of the deterioration depth over time as a linear function of the square root of
297 time, i.e. $K\sqrt{t}$. The proportionality with the square root of time is characteristic of a diffusion process.

298 The values of K for all cementitious materials are shown in Table 7 and are considered equal to
299 deterioration rates.

300 The deterioration rate obtained for the CAC material is 10 times lower than the deterioration rates for
301 the Portland cements (Table 7). The field tests from literature [8, 38, 39] showed a corrosion rate 4 times
302 lower for the CAC material in regard to CEM I cement. Consequently, this model overestimates the
303 better resistance of CAC materials, but it qualitatively consistent with observations. Moreover, the aim
304 of these simulations is to give chemical-based understanding of the better resistance of CAC cement
305 already observed with *in-situ* or laboratory tests. The partial dissolution of hydrogarnet shows that this
306 type of cement is constituted of hydrate resistant to acid conditions.

307 **5. Conclusion**

308 In this study, the effect of the cementitious material types on the deterioration obtained during 1 year of
309 sulfuric acid attack is evaluated with a chemical-reactive transport model.

310 The main results of the modeling highlight that the deterioration kinetic of the CAC materials is slower
311 than that of other cements (CEM I, CEM III, CEM IV and CEM V), as observed in several field tests.
312 This better resistance is mainly explained by the better thermodynamic stability in acidic conditions of
313 hydrogarnet compared to portlandite and C-S-H and to the ettringite precipitation which prevents the
314 penetration of sulfuric acid with a pore-blocking effect. But, this better resistance needs to be qualified
315 due to the ettringite precipitation, difficult to reconcile with some experimental studies.

316 The main perspectives for this sulfuric acid deterioration model are first, the implementation of a damage
317 model for the gypsum swelling and the ettringite precipitation for all the cementitious materials studied.

318 The second point to improve obviously concerns the consideration of the microorganisms which produce
319 sulfuric acid in sewer networks. Indeed, the factors controlling bio receptivity of cementitious materials,
320 which ultimately steers the acid production, are essential for modelling. Finally, the third point is the
321 inclusion of additional phases for blended Portland cements (blast furnace slag, pozzolans, and fly ashes)
322 in order to better represent these kinds of cements.

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329 **References**

330 [1] Brongers M., Koch G., Thompson N., Corrosion costs and preventive strategies in the United States,
331 Report FHWA-RD-01-156, 2001, Federal Highway Administration, Washington, DC.

332 [2] Zhang L., De Schryver P., De Gusseme B., De Muyneck W., Boon N. and Verstraete W., Chemical
333 and biological technologies for hydrogen sulfide emission control in sewer systems: a review, *Water*
334 *Research* 42 (2008): 1-12.

335 [3] Boon A.G., Specificity in sewers: causes, consequences and containments, *Water Science*
336 *Technology* 31 (1995): 237-253.

337 [4] Joseph A.P., Keller J., Bustamante H. and Bond P.L., Surface neutralization and H₂S oxidation at
338 early stages of sewer corrosion: Influence of temperature, relative humidity and H₂S concentration,
339 *Water Research* 46 (2012): 4235-45.

340 [5] Islander R.L., Deviny J.S., Mansfeld F., Postyn A. and Shih H., Microbial ecology of crown
341 corrosion in sewers, *Journal of Environmental Engineering* 117 (1991): 761-770.

342 [6] Okabe S., Odagiri M., Ito, T. and Satoh H., Succession of sulfur-oxidizing bacteria in the microbial
343 community on corroding concrete in sewer systems, *Applied and Environmental Microbiology* 73
344 (2007): 971-80.

345 [7] Davis J.L., Nica D., Shields K. and Roberts D.J., Analysis of concrete from corroded sewer pipe,

Grandclerc A., Dangla P., Gueguen-Minerbe M., Chaussadent T., *Modelling of the sulphuric acid attack on different types of cementitious materials, Cement and Concrete Research* 105 (2018) 126–133

346 *International Biodeterioration & Biodegradation* 42 (1998): 75 - 84.

347 [8] Alexander M. G. and Fourie C., Performance of sewer pipe concrete mixtures with Portland and
348 calcium aluminate cements subject to mineral and biogenic acid attack, *Materials and Structures* 44
349 (2010): 313-30.

350 [9] Pavlík V., Corrosion of hardened cement paste by acetic and nitric acids part I: Calculation of
351 corrosion depth, *Cement and Concrete Research* 24 (1994): 551 -62.

352 [10] Nielsen A.H., Hvitved-Jacobsen T. and Vollertsen J., Kinetics and stoichiometry of sulfide
353 oxidation by sewer biofilms, *Water Research* 39 (2005): 4119-25.

354 [11] Jensen H.S., Nielsen A.H., Hvitved-Jacobsen T. and Vollertsen J., Modeling of hydrogen sulfide
355 oxidation in concrete corrosion products from sewer pipes, *Water Environment Research* 81 (2009):
356 365-73.

357 [12] Jahani F., Deviny J., Mansfeld F., Rosen I.G., Sun Z. and Wang C., Investigations of sulfuric acid
358 corrosion of concrete. II: electrochemical and visual observations, *Journal of environmental engineering*
359 127 (2001): 580–584.

360 [13] Van der Lee G., De Windt L., Lagneau V. and Goblet P., Module-oriented modeling of reactive
361 transport with HYTEC, *Computers & Geosciences* 29 (2003): 265-75.

362 [14] De Windt L. and Devillers P., Modeling the degradation of Portland cement pastes by biogenic
363 organic acids, *Cement and Concrete Research* 40 (2010): 1165-74.

364 [15] Yuan H., Dangla P., Chatellier P. and Chaussadent T., Degradation modelling of concrete submitted
365 to sulfuric acid attack, *Cement and Concrete Research* 53 (2013): 267-77.

366 [16] Chalupecký, V., Fatima T., Kruschwitz J. and Muntean A., CASA-Report 12-01 January 2012.

367 [17] Yuan H., Dangla P., Chatellier P. and Chaussadent T., Degradation modeling of concrete submitted

Grandclerc A., Dangla P., Gueguen-Minerbe M., Chaussadent T., *Modelling of the sulphuric acid attack on different types of cementitious materials, Cement and Concrete Research* 105 (2018) 126–133

368 to biogenic acid attack, *Cement and Concrete Research* 70 (2015): 29–38.

369 [18] Bassuoni M.T. and Nehdi M.L., Resistance of self-consolidating concrete to sulfuric acid attack
370 with consecutive pH reduction, *Cement and Concrete Research* 37 (2007): 1070-84.

371 [19] Kawai K., Sako A., Ikuta T. and Ishida T., Deterioration of cement hydrates containing mineral
372 admixtures due to sulfuric acid attack, *In IIDBMC International Conference on Durability of Building*
373 *Materials and Components*, Istanbul, Turkey, 2008.

374 [20] Herisson J., Van Hullebusch E.D., Moletta-Denat M., Taquet P. and Chaussadent T., Toward an
375 accelerated biodeterioration test to understand the behavior of Portland and Calcium Aluminate
376 cementitious materials in sewer networks, *International Biodeterioration & Biodegradation* 84 (2013):
377 236-43.

378 [21] Jiang G., Wightman E., Bogdan C. D., Yuan Z., Bond P.L. and Keller J., The role of iron in sulfide
379 induced corrosion of sewer concrete, *Water Research* 49 (2014): 166-74.

380 [22] Gabrisova A., Havlica J. and Sahu S., Stability of calcium sulphoaluminate hydrates in water
381 solutions with various pH values, *Cement and Concrete Research* 21 (1991): 1023–1027.

382 [23] Herisson J., Guéguen-Minerbe M., Van Hullebusch E.D. and Chaussadent T., Behaviour of
383 different cementitious material formulations in sewer networks, *Water Science & Technology* 69 (2014):
384 1502.

385 [24] Schmidt M., Hormann K. and Hofmann F., Stability of concrete against biogenic sulfuric acid
386 corrosion, a new method for determination, *In Proceedings of the 10th international congress on the*
387 *chemistry of cement*, Gothenburg, 1997.

388 [25] Ehrich S., Helard L., Letourneux R., Willocq J. and Bock E., Biogenic and chemical sulfuric acid
389 corrosion of mortars, *Journal of materials in civil engineering* 11 (1999): 340–344.

390 [26] Miokono, D.H.E, Biodétérioration de mortiers avec une succession de bactéries sulfo-oxydantes

Grandclerc A., Dangla P., Gueguen-Minerbe M., Chaussadent T., *Modelling of the sulphuric acid attack on different types of cementitious materials, Cement and Concrete Research* 105 (2018) 126–133

391 neutrophiles et acidophiles, PhD at the University of Lille 1, 2013, 365 pages.

392 [27] Peyre Lavigne M., Bertron A., Auer L., Hernandez-Raquet G., Foussard J.N., Escadeillas G., Cockx
393 A. and Paul E., An innovative approach to reproduce the biodeterioration of industrial cementitious
394 products in a sewer environment. Part I: Test design, *Cement and Concrete Research* 73 (2015): 246-
395 56.

396 [28] NF P18-459, “Concrete – Hardened concrete test – Porosity and density tests”, French standard,
397 2010.

398 [29] Nilforushan M.R and Talebian N., The hydration products of a refractory calcium aluminate cement
399 at intermediate temperatures, *Iran. J. Chem. Eng* 26 (2007).

400 [30] Lamberet S., Guinot D., Lempereur E., Talley J. and Alt C., Field investigations of high
401 performance calcium aluminate mortar for wastewater applications, *Calcium aluminate cements,*
402 *proceeding of the centenary conference, Avignon, IHS BRE Press, 2008.*

403 [31] Damidot D., Lothenbach B., Herfort D. and Glasser F.P., Thermodynamic and cement science,
404 *Cement and Concrete Research* 41 (2011): 679-695.

405 [32] Dangla P., Thiery M. and Morandau A., Thermodynamic of incongruent solubility of C-S-H,
406 *Advances in Cement Research* (2015) (online version).

407 [33] Dangla P., Bil-2.4, A modeling platform based on finite volume/element method, doi:
408 10.5281/zenodo.1039729, 2017.

409 [34] Bazant Z.P. and Najjar L.J., Nonlinear water diffusion in nonsaturated concrete, *Materials and*
410 *structures* 5(1972): 3-20.

411 [35] Proceedings of the RILEM TC-211-PAE, Performance of cement-based materials in aggressive
412 aqueous environments, Springer (2013), ISBN 978-94-007-5419-3.

413 [36] Mori T., Nonaka M., Tazaki K., Koga M., Hikosaka Y. and Noda S., Interactions of nutrients,

Grandclerc A., Dangla P., Gueguen-Minerbe M., Chaussadent T., *Modelling of the sulphuric acid attack on different types of cementitious materials, Cement and Concrete Research* 105 (2018) 126–133

414 moisture and pH on microbial corrosion of concrete sewer pipes, *Water Research* 26 (1991): 29–37.

415 [37] Lee H.S., Ismail M.A., Woo Y.J., Min T.B. and Choi H.C., Fundamental study on the development
416 of structural lightweight concrete by using normal coarse aggregate and foaming agent, *Materials* 7
417 (2014): 4536-4554.

418 [38] Zhao H., Xiao Q., Huang D. and Zhang S., Influence of pore structure on compressive strength of
419 cement mortar, *Scientific World Journal*, Article ID 247058, 2014.

420 [39] Goyns A., Calcium aluminate cement linings for cost-effective sewers, *In International conference*
421 *on calcium aluminate cements*, 6317–6319, 2001.

422 [40] Alexander M. G., Goyns A. and Fourie C.W., Experiences with a full-scale experimental sewer
423 made with CAC and other cementitious binders in Virginia, South Africa, In Proceedings, *calcium*
424 *aluminate cements, the centenary conference*. IHS BRE Press, Bracknell, 279–292, 2008.

425

Cement	n _{CH} (mol/L)	n _{CSH} (mol/L)	n _{C3AH6} (mol/L)	n _{AH3} (mol/L)	Porosity (%)
CEM I	1.84	2.45	-	-	11
CEM III	1.18	2.83	-	-	18
CEM IV	0.75	3.10	-	-	16
CEM V	1.19	2.84			11
CAC	-	-	2	0	10

Table 1: Hydrate amounts and porosity for cement pastes based on CEM I, CEM III, CEM IV, CEM V cements, and CAC.

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Solid phases	Dissolution reactions	Thermodynamic constant (K)
Portlandite (CH)	Reaction involving calcium compounds $\text{Ca(OH)}_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$	$8.90 \cdot 10^{-6}$
Gibbsite (AH ₃)	Reaction involving aluminum compounds $\text{Al(OH)}_3 \rightleftharpoons \text{Al}^{3+} + 3\text{OH}^-$	$1.0 \cdot 10^{-68}$
Gypsum (C $\bar{\text{S}}\text{H}_2$)	Reaction involving calcium-sulfur compounds $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	$3.72 \cdot 10^{-5}$
AFm (C ₄ A $\bar{\text{S}}\text{H}_{12}$)	Reactions involving calcium-aluminum-sulfur compounds $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O} \rightleftharpoons 4\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 4\text{OH}^- + \text{SO}_4^{2-} + 6\text{H}_2\text{O}$	$3.71 \cdot 10^{-30}$
Ettringite (C ₃ A $\bar{\text{S}}_3\text{H}_{32}$)	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \rightleftharpoons 6\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 3\text{SO}_4^{2-} + 4\text{OH}^- + 26\text{H}_2\text{O}$	$2.80 \cdot 10^{-45}$
Hydrogarnet (C ₃ AH ₆)	Reactions involving calcium-aluminum compounds $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \rightleftharpoons 3\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 4\text{OH}^-$	$3.2 \cdot 10^{-21}$
C ₂ AH ₈	$2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_4^- + 2\text{Ca}^{2+} + 3\text{H}_2\text{O} + 2\text{OH}^-$	$2.8 \cdot 10^{-14}$
CAH ₁₀	$\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O} \rightleftharpoons 2\text{Al(OH)}_4^- + \text{Ca}^{2+} + 6\text{H}_2\text{O}$	$2.5 \cdot 10^{-8}$
C-S-H	Reaction involving calcium-silicon compounds $\text{C}_x\text{S}_y\text{H}_z \rightleftharpoons x\text{Ca}^{2+} + 2y\text{OH}^- + y\text{SiO}_2^0 + (z-x)\text{H}_2\text{O}$	See [15]
Silica gel (SH)	Reaction involving silicon compounds $\text{SH}_u \rightleftharpoons \text{SiO}_2^0 + u\text{H}_2\text{O}$	$1.74 \cdot 10^{-3}$

Table 2: Heterogeneous reactions taking place in the CaO-Al₂O₃-SiO₂-SO₃-H₂O system

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Dissociation reactions	Thermodynamic constant (K)
Reaction involving calcium compounds $\text{Ca(OH)}_2^0 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{Ca(OH)}^+ \rightleftharpoons \text{Ca}^{2+} + \text{OH}^-$	1 $1.66 \cdot 10^1$
Reactions involving silicon compounds $\text{SiO}_2^0 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4^0$ $\text{H}_4\text{SiO}_4^0 \rightleftharpoons \text{H}_3\text{SiO}_4^- + \text{H}^+$ $\text{H}_3\text{SiO}_4^- \rightleftharpoons \text{H}_2\text{SiO}_4^{2-} + \text{H}^+$ $\text{H}_2\text{SiO}_4^{2-} \rightleftharpoons \text{HSiO}_4^{3-} + \text{H}^+$	$1.94 \cdot 10^{-3}$ $1.55 \cdot 10^{-10}$ $4.68 \cdot 10^{-14}$ $1.0 \cdot 10^{-15}$
Reaction involving sodium compounds $\text{NaOH}^0 \rightleftharpoons \text{Na}^+ + \text{OH}^-$	1.5
Reaction involving potassium compounds $\text{KOH}^0 \rightleftharpoons \text{K}^+ + \text{OH}^-$	2.9
Reactions involving sulfur compounds $\text{H}_2\text{SO}_4^0 \rightleftharpoons \text{HSO}_4^- + \text{H}^+$ $\text{HSO}_4^- \rightleftharpoons \text{SO}_4^{2-} + \text{H}^+$	$1.0 \cdot 10^6$ $1.0 \cdot 10^{-2}$
Reaction involving aluminum compounds $\text{Al(OH)}_4^- \rightleftharpoons \text{Al}^{3+} + 4\text{OH}^-$	$6.2 \cdot 10^{-34}$
Reactions involving calcium-silicon compounds $\text{CaH}_2\text{SiO}_4^0 \rightleftharpoons \text{Ca}^{2+} + \text{H}_2\text{SiO}_4^{2-}$ $\text{CaH}_3\text{SiO}_4^+ \rightleftharpoons \text{Ca}^{2+} + \text{H}_3\text{SiO}_4^-$	$3.89 \cdot 10^4$ $1.56 \cdot 10^1$
Reaction involving calcium-sulfur compounds $\text{Ca}^{2+} + \text{SO}_4^{2-} \rightleftharpoons \text{CaSO}_4^0$ $\text{Ca}^{2+} + \text{HSO}_4^- \rightleftharpoons \text{CaHSO}_4^+$	$1.4 \cdot 10^{-3}$ $1.3 \cdot 10^1$

431 **Table 3: Homogeneous aqueous reactions taking place in CaO-Al₂O₃-SiO₂-SO₃-Na₂O-K₂O-H₂O**
 432 **system**

433

Solid phases	R _A (mol/L/s) for Portland cements	R _A (mol/L/s) for CAC cement
C $\bar{\text{S}}$ H ₂ (gypsum)	$1 \cdot 10^{-4}$	$1 \cdot 10^{-7}$
AFt	$1 \cdot 10^{-11}$	$1 \cdot 10^{-7}$
AFm	$1 \cdot 10^{-11}$	$1 \cdot 10^{-11}$
C ₃ AH ₆	-	$1 \cdot 10^{-8}$

434 **Table 4: Kinetic factors of the solid phases for the CaO-Al₂O₃-SO₃-H₂O system.**

435

Cement pastes	Deterioration depths (mm)
CEM I	2.0
CEM III	2.4
CEM IV	2.8
CEM V	2.2
CAC	0.2

436 **Table 5: Deterioration depths obtained for CEM I, CEM III, CEM IV, CEM V cements and**
 437 **CAC after 1 year of acid attack at 10^{-1} mol/L.**

Materials	Dissolved calcium amount (g/L)	Weight loss (%)
CEM I	90	37.5
CEM III	80	33.3
CEM IV	80	33.3
CEM V	80	33.3
CAC	35	14.6

438 **Table 6: Dissolved calcium contents obtained for CEM I, CEM III, CEM IV, CEM V cements,**
 439 **and CAC after 1 year of sulfuric acid attack at 10^{-1} mol/L.**

Materials	Corrosion rates (mm/year ^{0.5})
CEM I	0.10
CEM III	0.11
CEM IV	0.14
CEM V	0.10
CAC	0.01

440 **Table 7: Corrosion rates obtained for CEM I, CEM III, CEM IV, CEM V cements, and CAC.**

441

442 **Figure captions**

443 **Figure 1:** Concrete sewer and biodeterioration mechanisms. SRB are sulfate-reducing bacteria and SOB
 444 are sulfur-oxidizing bacteria.

445 **Figure 2:** Phase Diagram for the system CaO-Al₂O₃-SO₃-H₂O. This diagram is constituted of the
 446 simultaneous evolutions of the saturation indexes of AH₃ (β_{AH3}) and CH (β_{CH}) with the H₂SO₄
 447 concentration (a_{H2SO4}) in logarithmic scale.

448 **Figure 3:** Profiles of the solid phases (CH, C₃AH₆, AFt, AH₃, and C \bar{S} H₂ (gypsum)), of the calcium to
 449 silicon ratio and of the porosity, for cementitious materials based on CEM I, CEM III, CEM IV, CEM V
 450 cements, and CAC, after 1 year of acid attack.

451 **Figure 4:** Evolution of the porosity over depth for the cementitious materials based on CEM I, CEM III,
 452 CEM IV, CEM V cements, and CAC during 1 year of sulfuric acid attack at 10^{-1} mol/L. The black circles
 453 represent the point where porosity becomes superior to the initial porosity of each cementitious material.

454 **Figure 5:** Evolution of the deterioration depth for cementitious materials based on CEM I, CEM III,
 455 CEM IV, CEM V cements, and CAC over time, during 1 year of acid attack at 10^{-1} mol/L.

456 **Figure 6:** Dissolved calcium contents over time for cementitious materials based on CEM I, CEM III,
 457 CEM IV, CEM V cements, and CAC during 1 year of sulfuric acid attack at 10^{-1} mol/L.

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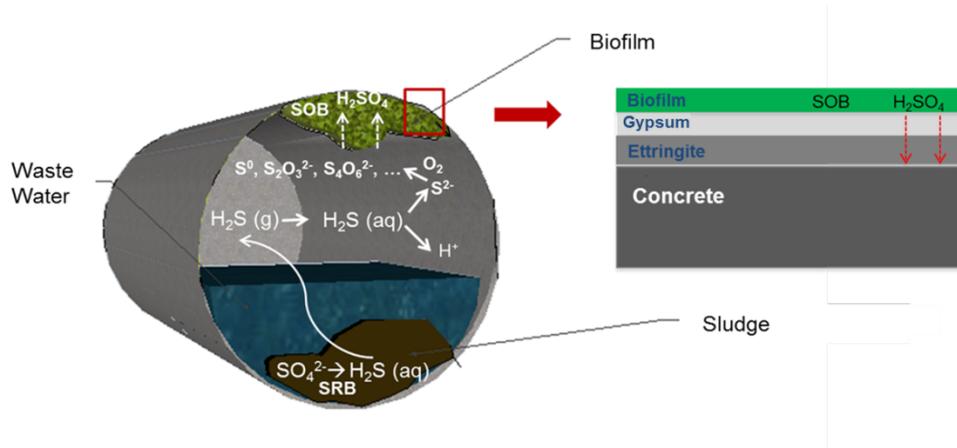
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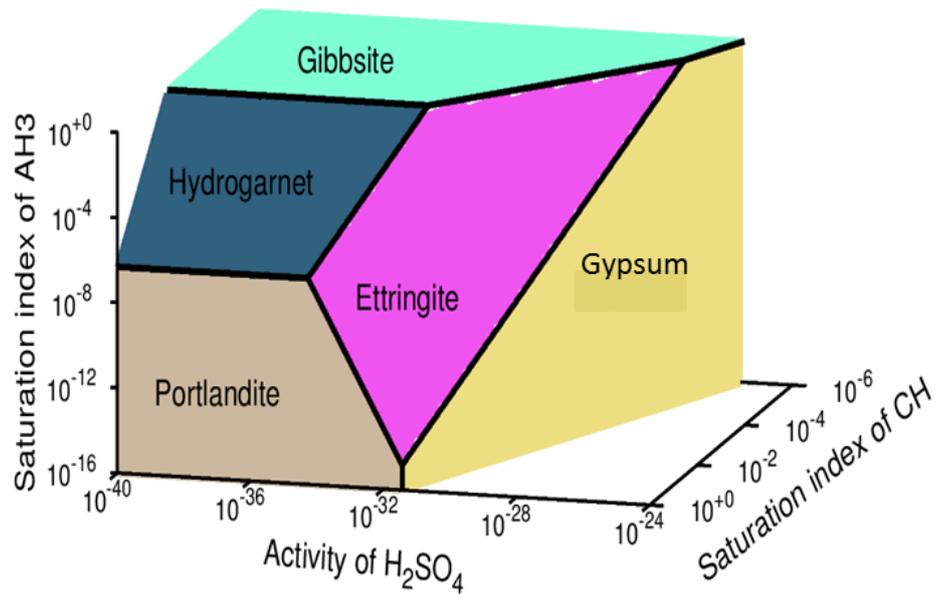
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463 **FIGURE 1.**



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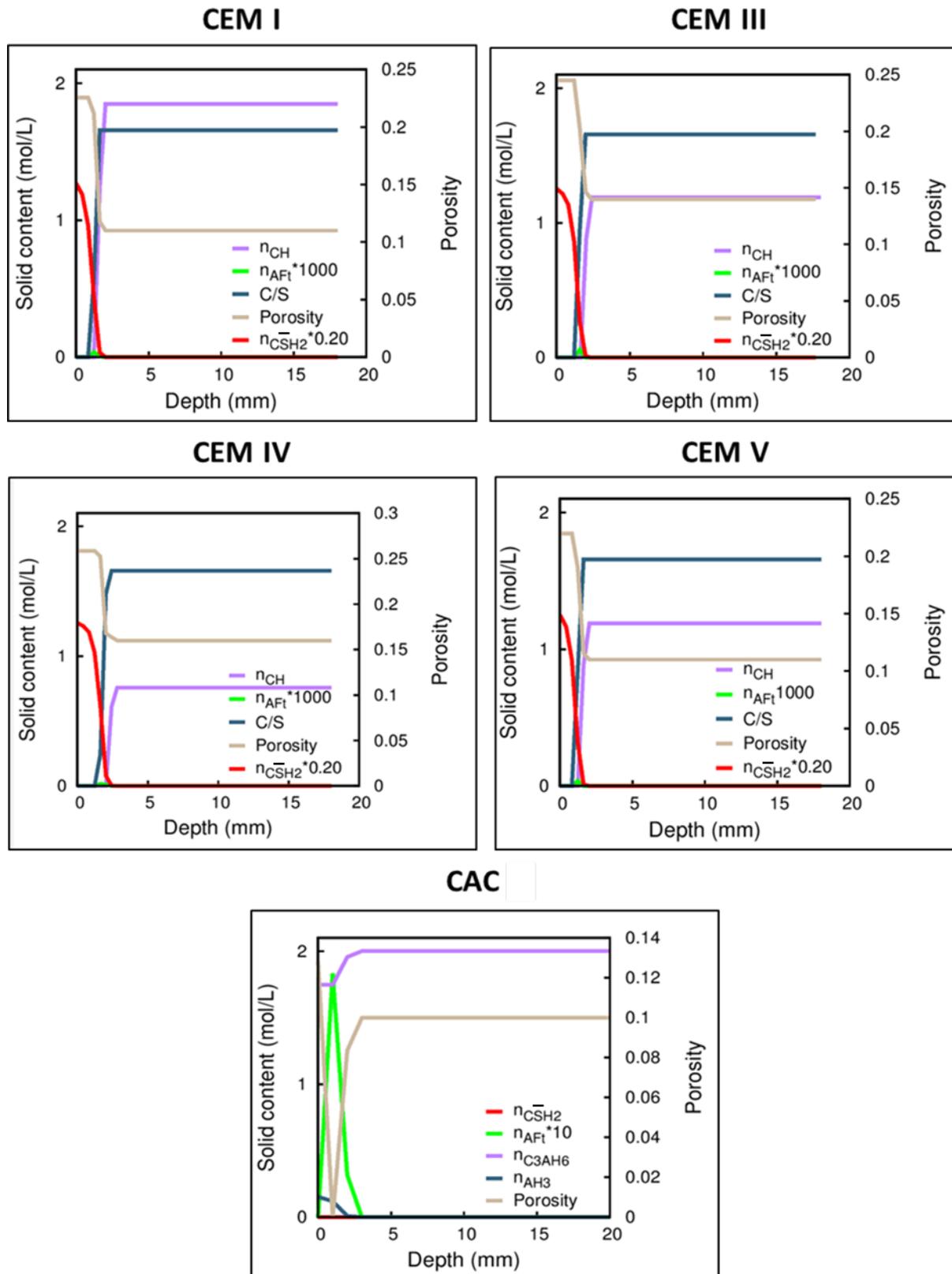
465 **FIGURE 2.**



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468 **FIGURE 3.**

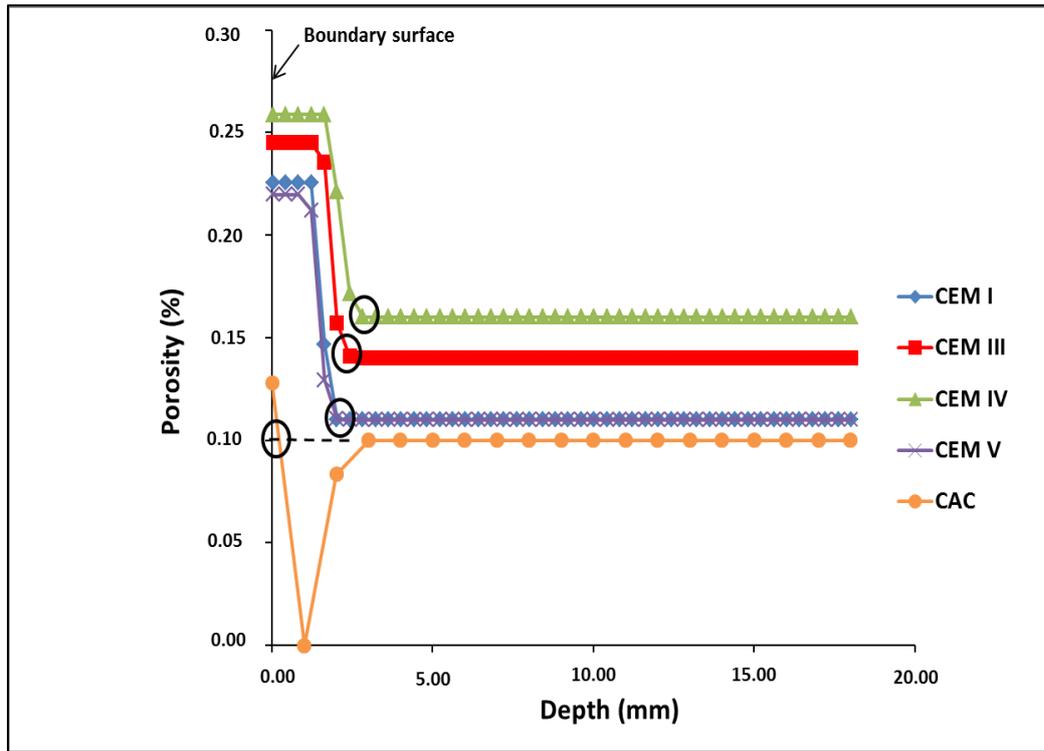


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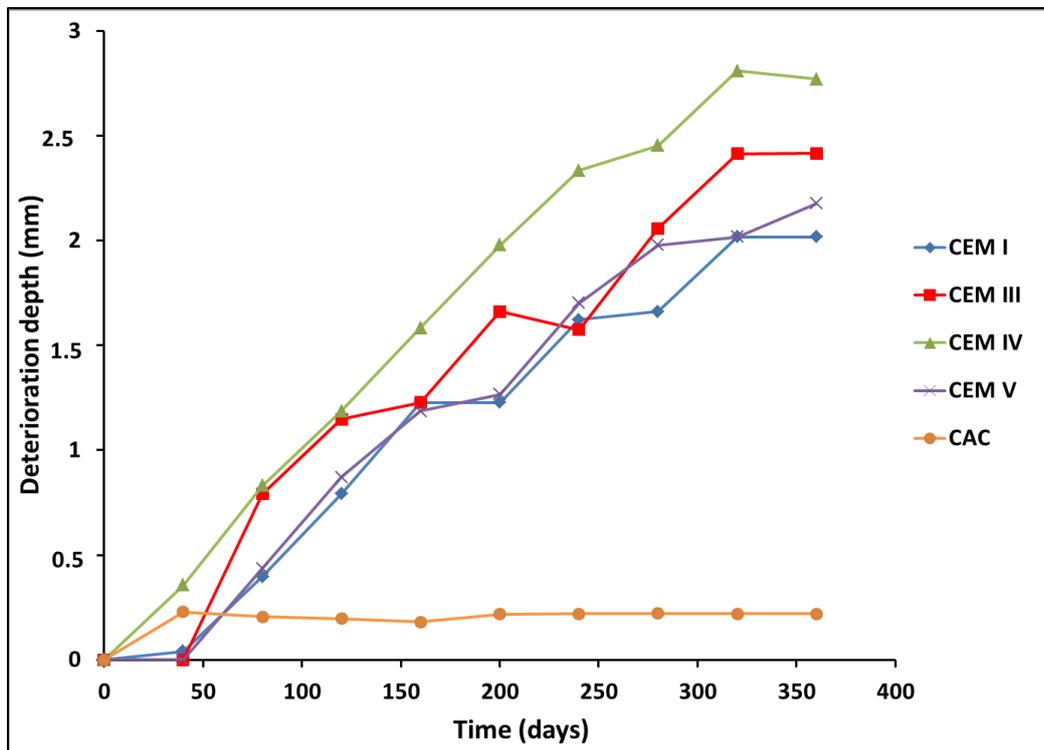
472 **FIGURE 4.**



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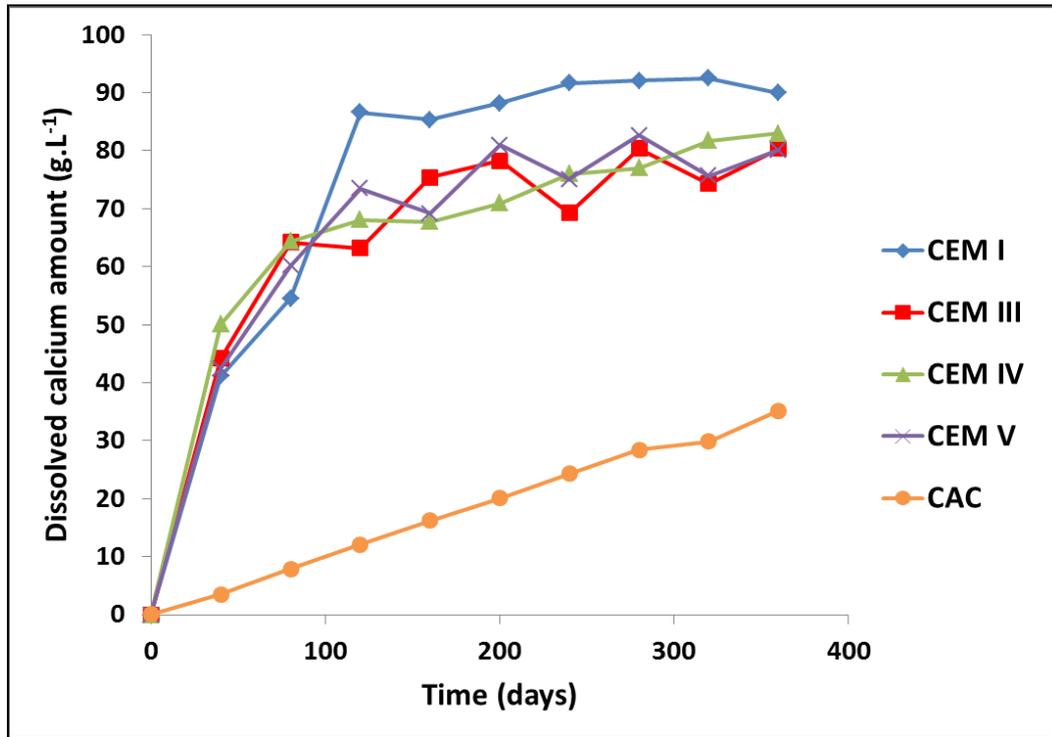
475 **FIGURE 5.**



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478 **FIGURE 6.**



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