

CEMENTAND CONCRETE

Cement and Concrete Research 32 (2002) 1451-1455

Deterioration of long-serving cement-based sandcrete structures in Nigeria

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Abstract

The fall in living standard of the Nigerian citizenry, starting from the mid-1980s, has encouraged massive importation of secondhand goods, most especially industrial machines, cars, motorcycles, etc. It is a well-known fact that the majority of these equipment are very inefficient and produce a lot of pollutants (Cl⁻, SO₂, CO₂, CO, N_xO_y, etc), particularly as a result of incomplete fuel combustion. The presence of these pollutants has contributed not only to the depreciation of the people's quality of life, but also to the degradation of cementbased structures' physicochemical, mechanical and aesthetic qualities. This paper is aimed at developing a deterministic model, based on a mechanism of cement corrosion, to predict the deterioration of cement-based structures in Nigeria. The developed model equation showed that intensive diffusion of pollutants takes place within 0- to 10-mm-depth of the sandcrete block. It represents the relationship between concentration of pollutant and depth of their penetration and gives a comparative measure of the ease of diffusion of the latter into the structure at various depths. Variation in the type of pollutant and possible reaction, including leaching need to be considered in order to develop an acceptable model. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Pollutants; Kinetics; Degradation; Hydration products; Diffusion

1. Introduction

The compressive strength of cement-based structures is expected to increase steadily with age. However, this statement may not be true for many structures, especially those serving in aggressive environments. In some areas, most cement-based structures were found to develop microcracks within a few years after construction, despite the fact that acceptable standards were observed. It has been proved by various researchers that long exposure of cement-based structures to aggressive medium containing acids, alkalis and salts immensely enhance their physicochemical and mechanical properties' deterioration [1].

Results of various researchers have shown that the weak point in hardened cement microstructure remains the presence in it of soluble and reactive Ca(OH)₂ [2]. Much work has been done in investigating the mechanism of various destructive processes responsible for cement-based structure deterioration [2-4]. In his work [2], Moskivic formulated the basic points for developing the theory of cement-based structure deterioration. It was established that in order to qualitatively assess the kinetics of corrosion process, it is necessary to study the internal diffusion of an aggressive substance, the formation on the cement-based structure surface, layer of the reaction products, crystallization of corrosive components and products of their interaction with hardened cement minerals in the voids and other processes. This paper is aimed at developing a deterministic model equation based on the mechanism of cement corrosion to predict the deterioration of cement-based sandcrete commonly used as a building material in Nigeria.

2. Mathematical modelling of pollutants' diffusion into sandcrete structure

The sandcrete block consists of a mixture of cement and coarse sand mixed with water to obtain a normal consistency. The mix is then poured into a form and vibrated. Sandcrete structures may have a porosity of more than 25% depending on the extent of vibration. The sandcrete block forms the major construction material in the Nigeria building industry. Nigeria is a developing country. Pollution problems associated with heavy industrialization are today being experienced globally. However, all mitigating features to combat the trend

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PII: S0008-8846(02)00802-5

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of events have failed in the developing world as a result of these countries being converted to dumping grounds for used and inefficient machinery. Today no community is free from gaseous pollutants from automobiles and motorcycles manufactured using outdated technologies. Consequently, the major pollutants of our cities include products from incomplete burning of hydrocarbon fuel, such as CO₂, SO₂, Cl⁻, CO, NO_x, etc. The presence of these pollutants has contributed not only to the depreciation of the peoples' quality of life, but also to the degradation of cement based structures' physicochemical, mechanical and aesthetic qualities [1].

These pollutants affect the properties of cement-based structures only when they are in direct contact. This is possible through adsorption and diffusion of these pollutants into the structure's matrix. Therefore, the rate of the pollutants' diffusion into the matrix will determine to a great extent the longevity of the cement-based structure. This is the focus of this research, with particular reference to long-serving sandcrete structures in Nigeria.

2.1. Basic assumption

The following assumptions were made to facilitate the derivation of the deterministic model equation.

- The cement block is well compacted and therefore available interpore space is assumed to be spherical if well compacted.
- 2. Fick's law holds for the diffusion mechanism.
- 3. The product of the chemical reaction is retained on the surface of the particles in a monomolecular layer.
- 4. Diffusion is predominantly in one direction of gas flow, except for particles at the edges.
- 5. The pollutant gases obey the general gas law
- 6. Surface flux is based on the total area of the solid particles perpendicular to the direction of diffusion.

By analogy to Fick's law, the molar rate per unit of pore surface N_s is (Eq. (1)) [6-8]

$$N_{\rm s} = -D_{\rm s} \frac{\mathrm{d}C_{\rm s}}{\mathrm{d}r} \tag{1}$$

where C_s is the surface concentration (mol gas/m³) and r is the depth of pollutant gas penetration (m) [8].

For diffusion in a porous solid the surface flux $(N_{\rm s})_{\rm e}$ should be based on the total area perpendicular to the direction of diffusion on the coordinate r

$$(N_{\rm s})_{\rm e} = -\rho_{\rm b} D_{\rm e} \frac{\mathrm{d}C_{\rm A}}{\mathrm{d}r} \tag{2}$$

where $D_{\rm e}$ is the effective diffusivity per unit of the total cross-sectional area, C the moles adsorbed per gram solid (mol/g) and $\rho_{\rm b}$ the density of the block.

The equilibrium concentration of the net rate of adsorption of gases on the solid, according to Langmuir's law can be represented as

$$C_{\rm A} = K \bar{C}_{\rm m} C_{\rm g} \tag{3}$$

where C_A is the adsorbed concentration on the solid surface (mol/g), $\bar{C}_{\rm m}$ is the concentration corresponding to complete monomolecular layer on the solid, $C_{\rm g}$ the concentration of adsorbable component in the gas phase (it is proportional to P) and K is the linear form of equilibrium constant (m³/g).

Due to the long exposure of the sandcrete blocks under investigation, equilibrium is assumed to exist between the gas and the surface concentration. Eq. (3) can be represented as

$$C_{\rm A} = K_{\rm A} \bar{C}_{\rm m} C_{\rm g} = K_{\rm A} \frac{p y_{\rm A}}{R_{\rm o} T} \tag{4}$$

Substituting Eq. (4) into Eq. (2) gives Eq. (5).

$$(N_{\rm s})_{\rm e} = -\frac{p}{R_{\rm e}T} K_{\rm A} D_{\rm e} \rho_{\rm b} \frac{\mathrm{d}y_{\rm A}}{\mathrm{d}r} \tag{5}$$

The total surface flux is (Eq. (6))

$$(N_{\rm s})_{\rm t} = N_{\rm s} + (N_{\rm s})_{\rm e}$$
 (6)

Therefore

$$(N_{\rm s})_{\rm t} = -\frac{p}{R_{\rm g}T}(D + \rho_{\rm b}K_{\rm A}D_{\rm s})\frac{\mathrm{d}y_{\rm A}}{\mathrm{d}r}$$
(7)

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$$(N_{\rm s})_{\rm t} = -(D + \rho_{\rm b} K_{\rm A} D_{\rm s}) \frac{\mathrm{d} C_{\rm A}}{\mathrm{d} r} \tag{8}$$

Therefore

$$(D_{\rm e})_{\rm t} = D + \rho_{\rm b} K_{\rm A} D_{\rm s} \tag{9}$$

The overall rate of reaction W_A of component A on the structure is (Eq. (10))

$$W_{\mathbf{A}} = (N_{\mathbf{A}})_{+} V \tag{10}$$

where V is the volume of the structure = length \times width \times depth of pollutant gas penetration (LBr). Therefore, Eq. (8) becomes

$$W_{\rm A} \frac{\mathrm{d}r}{r} = -\mathrm{LB}(D + \rho_{\rm b} K_{\rm A} D_{\rm s}) \mathrm{d}C_{\rm A} \tag{11}$$

$$W_{\rm A} \int_{r=0}^{r=r} \frac{\mathrm{d}r}{r} = {\rm LB}(D + \rho_{\rm b} K_{\rm A} D_{\rm s}) \int_{c=c_{\rm A}}^{c=0} \mathrm{d}C_{\rm A}$$
 (12)

$$W_{\rm A} \ln r = LB(D + \rho_{\rm b} K_{\rm A} D_{\rm s}) C_{\rm A} \tag{13}$$

Let LB=a constant and then assume that no diffusion took place, except on the perpendicular surface to the

direction of gas flow. In the linear form y = mx, Eq. (13) can be presented as

$$C_{\rm A} = \frac{W_{\rm A}}{D_c} \ln r \tag{14}$$

taking

$$D_{\rm c} = LB(D + \rho_{\rm b} K_{\rm A} D_{\rm s})$$

where lnr is the natural logarithm of the depth of pollutant gas penetration.

Eq. (14) is the modeling equation for the research.

3. Experiment

The samples A (20 years old) and B (15 years old) were collected from exposed long-serving sandcrete blocks used for fencing at highly industrialized layouts A and B in Lagos, Nigeria. The choice of samples was based on the age of the fence and centrality of the structure in the two industrial layouts. All samples were collected by drilling, using a hand-drilling machine, equal distances into the block wall used for the fence; at the top, middle and ground levels. The control sample (1 day old) was collected from a block industry in Minna; about 500 km north of Lagos. All samples were produced by mixing sand and cement with potable water. The mixture with moisture content of 30-40% is then poured into a mould and compressed either manually or vibrated mechanically. Minna is a city with practically no functional large-scale industry; consequently, except from automobiles and the homes, not many pollutants are generated. Each of the collected samples was ground in a ceramic-lined mill to a fineness of about 68% residue on an 80- μ m-size mesh. All the chemical analyses were conducted according to Refs. [5,9].

4. Results and discussion

Results of the experiments are presented in Figs. 1 and 2 and Table 1. From Eq. (14), $C_{\rm A}$ is directly proportional to the natural logarithm of the depth of pollutant penetration, lnr. The gradient of the line so obtained will be equal to $W_{\rm A}/D_{\rm C}$. $W_{\rm A}$ for a given pollutant is calculated from the quantity of reaction product deposited in the sandcrete over the experimental period. The results of analysis of the rate of reaction for the various pollutants are presented in Tables 2 and 3.

The CO₂, SO₂ and Cl⁻ were the pollutants investigated in this paper. Analysis, based on the quantity of deposition and rate of penetration, showed that the maximum concentration of the pollutants investigated (SO₂, CO₂ and Cl⁻) was dependent on the level and depth of sampling (Figs. 1 and 2 and Table 2). The concentration of CO_3^2 and Cl in the block increased by 3–10.5 and 1–2 times, respectively, over a 15- to 20-year period. The significant disparity in the CO_3^2 concentration maybe connected to the conversion of the insoluble CaCO₃ to soluble Ca(HCO₃) and its subsequent leaching [2–4]. The concentration of SO₃ increased by 1.6– 6.5 times for sample A and 2.3–6.0 times for B in comparison to the control sample. The Ca(OH)₂ concentration during this 15-20 years decreased only by about 1.4 times for B and 1.3 for A. The mechanism of cement mineral hydration showed that the extent of hydration tends to 1 after many years [10]; with only about 60% extent of hydration attained after 180 days even for fast-hydrating cement [11]. The free Ca(OH)₂ is continuously utilized through various reactions such as in the

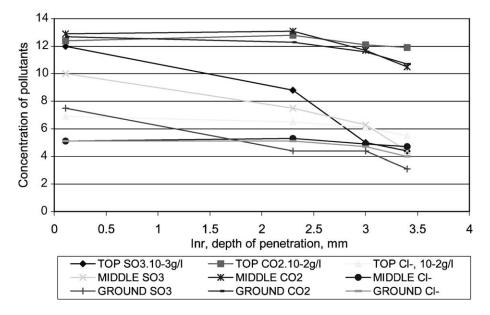


Fig. 1. Concentration of pollutants versus depth of penetration in Site A.

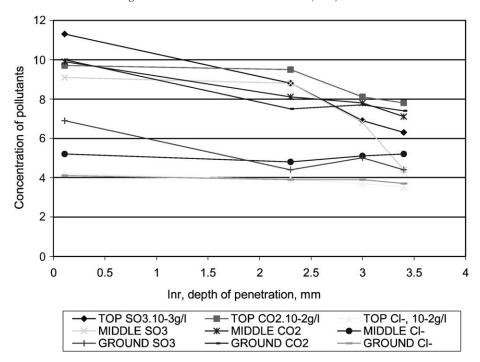


Fig. 2. Concentration of pollutants versus depth of penetration in Site B.

30.0

presence of SO_3 , or CO_2 or Cl^- and water to produce gypsum, $CaCO_3$ ($Ca(HCO_3)_2$) and $CaCl_2$, respectively. In the presence of active SiO_2 , $Ca(OH)_2$ will react to produce various solid solutions of C-S-H [11].

The porous nature of the sandcrete block ensures that the increased volume experienced as increased stress during the formation of ettringite in the course of the reaction involving CaSO₄·2H₂O and calcium aluminate/ferrite hydrates is completely adsorbed. Unlike SO₂ pollutant and sometimes CO₂, Cl⁻ will always lead to increased porosity of the structure as the resultant soluble CaCl₂ or unstable monochloroaluminates can be easily removed via leaching.

Analysis of Table 2 showed that the rate of deposition of all the pollutants investigated is higher at the outer surface. There is no linear relationship between the rate of reaction and the depth of the pollutants' penetration. The rate of deposition of CO_2 in the sandcrete block was the highest irrespective of the depth or age of the samples. The CO_3^2 was fairly well distributed in all the depths investigated, with 4–25% variation between the outer and the inner layers. It is followed by SO_3 ; however, the extent of variation was relatively high: 37% to 57%. The extent of

Table 1 Averaged concentration of Ca(OH)₂ at different depths

Depth, r (mm)	Sample concentration (\times 10 ⁻² g/l)			
	Control	A	В	
0.9	9.3	8.0	7.7	
10.0	10.4	8.3	7.8	
20.0	10.7	8.5	7.9	

variation for Cl⁻ was the least. The difference in the various rates of reactions involving SO₂, Cl₂ and CO₂ for samples A and B showed that the observed Ca(OH)₂ content (Table 1) could not have been the products of the primary reactions of cement minerals' hydration [10,11]. Their continuous presence is the resultant of various secondary reactions involving the cement minerals' hydrates and pollutants introduced into the sandcrete block.

Table 2
Rate of various pollutants' deposition in sandcrete block

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	Level						
Depth, r (mm)	Тор		Middle	Middle		Ground	
Rate of SO ₃ depos	sition, × I	$10^{-9} (g/l)$)/h at dept	hs, for samp	oles from :	sites A	
and B							
0.9	69	87	59	72.5	44	53	
10.0	50	67	43	67	25	33	
20.0	28	53	36	48	25	38	
30.0	25	48	25	33	17	33	
Rate of CO_2 depose	sition, ×	$10^{-8} (g/l)$)/h at dept	hs, for sam	oles from .	sites A	
0.9	72	75	75	76	73	77	
10.0	74	73	76	63	71	73	
20.0	70	63	68	60	67	59	
30.0	69	60	61	55	62	57	
Rate of Cl - depo and B	sition, ×	10 ^{- 8} (g/l	!)/h at dep	ths for samp	oles from .	sites A	
апа <i>В</i> 0.9	40	49	3.0	40	30	32	
10.0	38	46	3.1	37	30	30	
20.0	35	46	2.8	39	27	30	
20.0	33	40	2.8	39	21	30	

2.7

23

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Table 3
Diffusivity coefficients of pollutants in samples at different depths and levels

	Level							
	Тор		Middle		Ground			
Depth, mm	A	В	A	В	A	В		
Diffusivity of SO_3 , $\times 10^{-6}$ mm/h at depths, for samples from sites A and B								
0.9 - 10	14.3	19.2	10.0	24.0	19.2	25.0		
10 - 20	4.05	5.16	4.09	6.64	*	*		
20 - 30	0.17	3.3	2.31	2.5	2.46	3.3		
Diffusivity of CO ₂ , $\times 10^{-6}$ mm/h at depths, for samples from sites A and B								
0.9 - 10	*	25	*	17.3	11.8	3.84		
10 - 20	4.0	5.0	4.0	7.0	4.0	4.83		
20 - 30	0.5	4.0	2.3	2.86	2.22	2.66		
Diffusivity of Cl^- , $\times 10^{-6}$ mm/h at depths, for samples from sites A and B								
0.9 - 10	12.0	25.0	*	10.0	*	25.0		
10 - 20	5.88	*	5.26	*	5.26	*		
20 - 30	2.0	2.0	3.3	*	2.28	2.0		

^{*} Shows equilibrium or reverse in the relative rate of product deposition in the sandcrete depths. This retards the diffusivity of the pollutants.

The outer layer diffusivity values for all the pollutants investigated were, for most cases, higher than those of the interior (Table 3). However, the observed disparities of D values between the layers' depth might be connected with the nonuniform rates of leaching of the reaction products and the resultant exposure of the cement minerals' hydrates surfaces.

Among the pollutants investigated SO_2 has the highest D values; however, the high porosity of the sandcrete block structure coupled with the small percentage concentration in the mix made its degrading effect very minimal. The degrading effect of CO₂ was enhanced by its relative abundance in the atmosphere. The deposition of CaCO₃ on the outer surface of the sandcrete block reduces the penetration of CO_2 into the structure. The nonuniformity in the D values with increasing depth could be attributed to inconsistency in the diffusion of pollutant and the transformation of the resultant reaction product CaCO3 to Ca(HCO3)2 and the possible leaching from the structure. Chloride (Cl⁻) showed serious inconsistencies in the D values. This could be attributed to the relative ease with which the product of C-S-H and Cl $^-$ reaction is leached from the structure. The deterioration mechanism in the serving structure could therefore be considered dependent on the:

- (a) In-built or self-destructive mechanism, which in this case include the quality of the cement, sand and water and the block production technique.
- (b) External or prevailing environmental conditions and
- (c) The extent of interaction of (a) and (b), to be defined by time.

These factors are adequately represented in the model Eq. (14). For any structure; even when serving in the same locality, the above-mentioned factors cannot be the same

due to variation in especially the internal factors. This could account for observed variations in data presented in Tables 2 and 3

In general the study showed that the overall pollutants' D values in the sandcrete structure is dependent on the type of pollutant and its reaction with cement minerals, and the rate of leaching of these products. However, the developed mathematical model can serve as a comparative tool to determine the ease of diffusion of pollutants into the serving sandcrete block. The higher the diffusivity, the lesser will be the expected mechanical strength of the structure.

5. Conclusion

The developed model equation showed that intensive diffusion of pollutants takes place within 0-10 mm depth of the sandcrete block. It represents the relationship between the concentration of pollutant and depth of their penetration and gives a comparative measure of the ease of diffusion of the latter into the structure at various depths. Variation in the type of pollutant and possible reaction, including leaching, need to be considered in order to develop an acceptable model.

Acknowledgments

I wish to acknowledge the Federal University of Technology Board of Research and the Third World Academy of Sciences, Italy for sponsoring this research.

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