FEDERAL UNIVERSITY OF TECHNOLOGY MINNA

DUALITY OF CEMENT- BASED STRUCTURES: MITIGATING GLOBAL WARMING AND BUILDING COLLAPSE

By

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INAUGURAL LECTURE SERIES 13

5TH MARCH, 2009

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This book is dedicated my wife Mrs. Helen E. Odigure and children; Hilda, John, Josephine and Joseph and most especially, to Almighty God for His unfailing love.

The Chairman
Vice Chancellor
Director-Generals
Deputy Vice Chancellors
Members of Council
The Registrar
Principal Officers of the University
Deans of Schools
Distinguished Professors and Scholars
Directors of Centers
Heads of Departments
Members of the Academia
Friends of the University
Staff of the University
Distinguished Guests
Gentlemen of the Press
Great Nigerian Students
Ladies and Gentlemen

I also want to acknowledge the presence of our God, the ALMIGHTY Father in this gathering.

INTRODUCTION

The concept of this work and my sojourn in academy is a product of the contrast in my University education and my working environment; a contrast between a robust academic abundance and poverty. The Nigerian education is presently driven by theory. This presentation is structured in triple helix; chemical analyses developing reaction mechanism/models predictable outcomes. The global relevance of this work stems from the developed models.

There were 2.35 billion tons of cement used in 2007 and demand is increasing at 130 million tons per year worldwide. 1.4 billion tons of cement is produced and used in China in 2007[1]. It is estimated that Nigeria local

installed capacity should be in the region of 6 or 7 million metric tonnes at the moment. The total national demand for cement is put at about 15 million metric tonnes while production is in the neighborhood of 6.2 million metric tones and 8 million metric tonnes are imported in bulk and re-bagged in Nigeria.

CO_2 emissions are 27 billion tons per year worldwide[2]. The entire US production of CO_2 is now 6 billion tons. Current cement production process technology releases about 5 billion tons of CO_2/year. The growing atmospheric carbon dioxide concentration will reach 550 ppm by the end of the century if left unchecked. The Kyoto agreement calls for reduction of CO_2 emissions by industrial nations to 5% below 1990 levels between 2008 and 2012.

Cement-based products constitute the largest surface area man-made structure apart from naturally occurring sea and forest land. The World trade center used 955,000 tons of cement and 200,000 tons of steel and had 10 million square feet of space. The world commercial building business is a trillion dollar industry making billions of square feet each year[3]. Shanghai had 3000 buildings over 24 meters (12 stories) high by 2000 meters and a hundred of which are over 100 meters high[4]. New 5-7 MW and larger wind turbines are over 120 meters tall and require hundreds of tons of cement for each construction. There are also demands for hundreds of new airports. 10.8 million tons of cement used for the Three Gorges Dam.
Cement costs between $90-150/ton[3,4].

The various ways to reduce CO_2 emissions include developing revolutionary emission free energy production processes, sequestration by artificial carbonate rocks, forestation of desert land etc. Various goals for avoiding climate change suggest reducing those emissions by 7 billion tons/year or more aggressively to half the current level. Calera, a Vinod Khosla funded company, is starting up a pilot plant for a new type of cement and process that would remove 1 ton of CO_2 from the air to make 1 ton of cement. The plan is to have 100 plants producing up to 1 billion tons of the new cement by 2015.

This technology has the potential to accelerate cement production by 10-40 billion tons/year instead of 4 billion tons per year (under normal growth) by 2020. It would be a major form of productive carbon sequestering[3,5,6].

Robert Niven, founder of Halifax-based Carbon Sense Solutions[7], says that his company's process would actually allow precast concrete to store carbon dioxide. The company takes advantage of a natural process; carbon dioxide is already reabsorbed in concrete products over hundreds of years from natural chemical reactions. Freshly mixed concrete is exposed to a stream of carbon-dioxide-rich flue gas, rapidly speeding up the reactions between the gas and the calcium-containing minerals in cement (which represents about 10 to 15 percent of the concrete's volume). The technology also virtually eliminates the need for heat or steam, saving energy and emissions[1,7,8].

Work is expected to begin on a pilot plant in the province of Nova Scotia this summer, with preliminary results expected by the end of the year. If it works and is widely adopted, it has the potential to sequester 20 percent of all cement-industry carbon-dioxide emissions[7].

The idea of concrete carbonation has been around for decades but has never been economical as a way to strengthen or improve the finished product. In the late 1990s, researchers showed how carbon dioxide could be turned into a supercritical fluid and injected into concrete to make it stronger, but the required high pressures made the process too energy intensive. Carbon Sense Solutions claims to achieve the same goal but under atmospheric pressure and without the need for special curing chambers

It is well documented that all concrete absorbs carbon dioxide over time if left to cure naturally--but only up to a point. The gas usually penetrates the first one or two millimeters of the concrete's surface before forming a hard crust that blocks any further absorption. Naik says that something as simple as using less sand in a concrete mix can increase the porosity of the finished product and allow more ambient carbon dioxide to be absorbed into the concrete. It's simpler than Carbon Sense Solutions' accelerated curing

process and can be applied to a much larger market[8].

Other groups are working at utilizing the emissions from the cement-making process itself. Researchers at MIT are seeking new ingredients in cement that are less energy intensive, while companies such as Montreal's CO_2 Solution have an enzymatic approach that captures carbon-dioxide emissions from cement-factory flue stacks, converts the greenhouse gas into limestone, and feeds it back into the cement-making process. Calera, backed by venture capitalist Vinod Khosla, even claims that it can remove a ton of carbon dioxide from the environment for every ton of cement it produces.

Cement-based structures are hardly ever built under ideal conditions, so, for variety of reasons, defect may occur as the concrete is being cast or after some time[9]. The factors that initiate corrosion of cement-based structure could be physical or chemical in nature[10,11]. Reactions occurring internally in cemented systems may have significant adverse effect on concrete structure[10-15]. 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 micro-cracks within a few years after construction despite the fact that acceptable standard were observed[11]. Various researchers have proved that long exposure of cement-based structures to aggressive medium containing acids, salt and alkalis immensely enhance their physicochemical and mechanical properties deterioration[10-16].

Reactions occurring internally, such as alkali aggregate reaction give cause for concern, because this type of deterioration does occur in non-aggressive environment[15]. The potential for reaction is conditioned by chemical and mineralogical nature of the concrete system components; cement-aggregate - water composition, as well as prevailing environmental condition - temperature, humidity, etc. Results of various researchers have shown that the weak point in hardened cement microstructure remains the presence in it

of soluble and reactive $Ca(OH)_2$[10].

The basic origin of the chemical energy potential involved in alkali-aggregate reaction is associated with the thermodynamically unstable nature of the reaction products involving the siliceous aggregate materials and the alkaline mineral hydrates from the cement[17]. This to a large extent defines the cement-based structures matrix rheology and morphology. For structures exposed to seasonal wetting or flooding by water their chemical deterioration will depend on the extent of solubility of the mineral hydrates and possible migration through the various hardened matrix. Such migration of the soluble salts or hydrates will be enhanced by contact of such structure to a wet earth base/foundation. This determines the stability of the cement based structure it development of microcrack or even collapse. Presented in Figures 1- 6 are common pictures of cement-based structure failures.

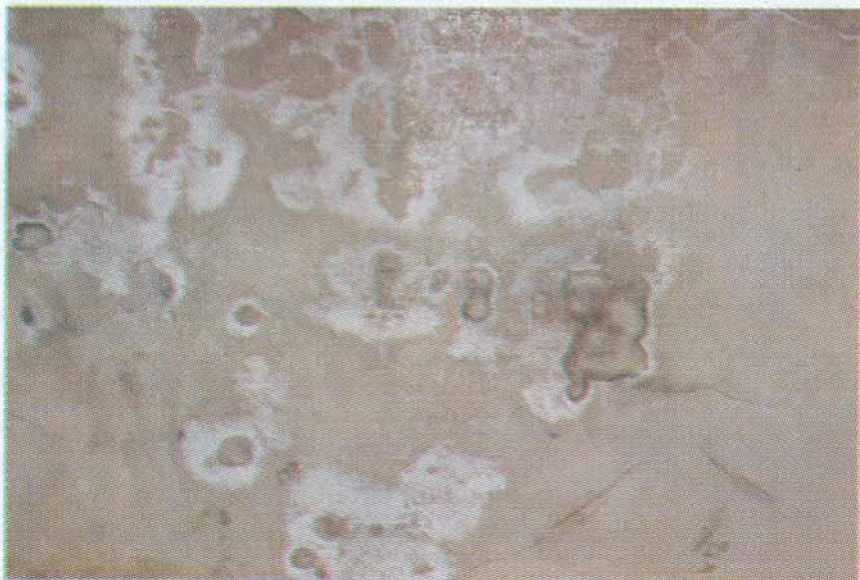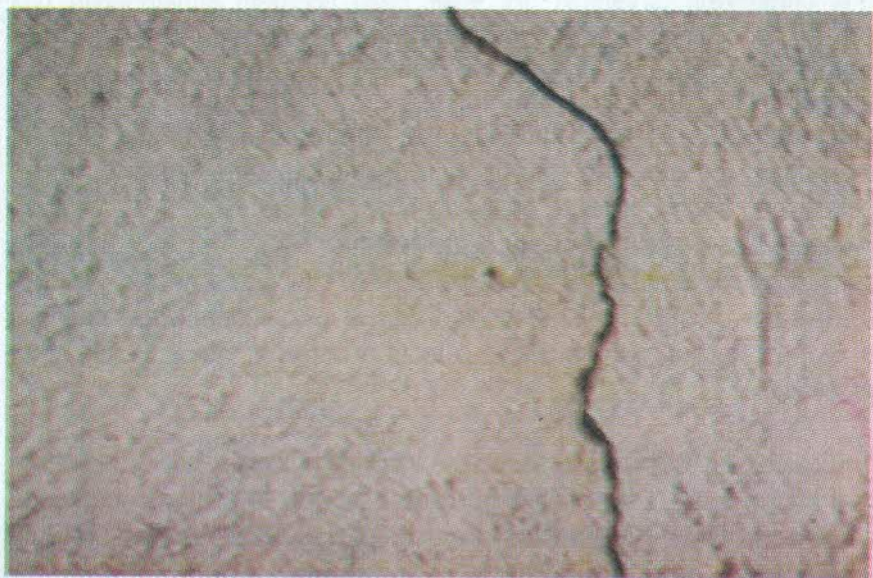Figure 1: Poor adhesion at paint cement mortar interphase

Figure 2: Cracking of sandcrete wall

Figure 3: Cracked wall

Figure 4 Saltation of cement-based wall
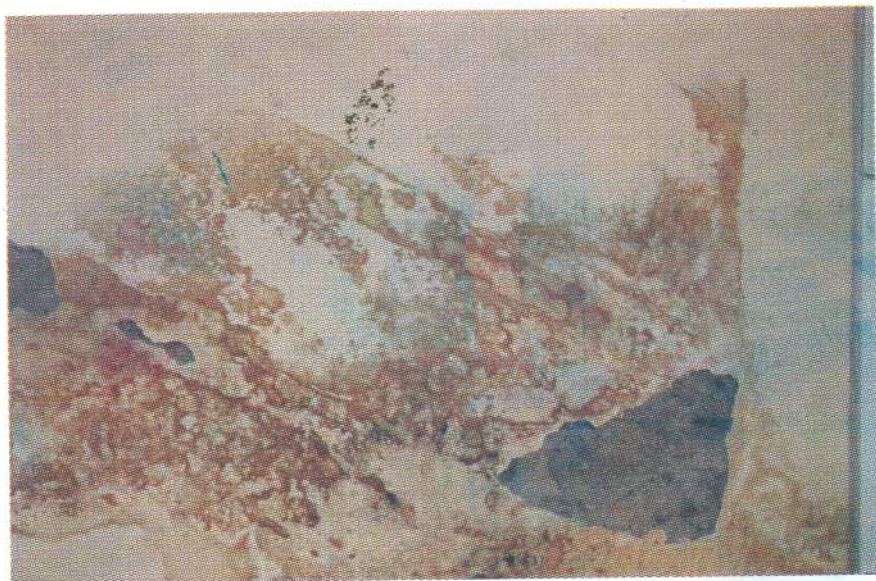

Figure 5: Cracked wall

Figure 6: Poor adhesion of cement binder and aggregate leading to dissociation of matrix.

Much work has been done in investigating the mechanism of various destructive processes responsible for cement-based structure deterioration[10-12]. In his work Moskivic formulated the basic points for developing the theory of cement-based structure deterioration[10]. 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, layering of the reaction products, crystallization of corrosive components and products of their interaction with hardened cement minerals in the voids and other processes.

The basic characteristics of sandcrete block commonly used in Nigeria are well known to us. Essentially it is made from coarse sand as aggregate, cement and water. The resultant mix is compacted at various pressures and allowed to dry.

The main aim of this work is to highlight based on chemical investigations the mechanism of carbon dioxide and other pollutants sequestration and deterioration of cement based structure. Various works aimed at understanding the mechanism of the processes involved are presented for discussion. Structural failure of cement-based structure often experienced as building collapsed will be discussed based on the proposed mechanism of deterioration.

CHEMICAL EVALUATION OF SANDCRETE STRUCTURE DETERIORATION

Samples were collected from non-industrial areas of Kaduna, capital of Kaduna State in Nigeria, specifically from the Kurmi mashi I & II and Ungwan Mu'azu I & II areas. The structures are located in abandoned market site constructed 5 and 6yrs ago respectively. Samples were collected from three levels on both sides across and along the cracked line. The controlled samples were also collected from structure located in the same area. Additional experiments were conducted on local indigenous cement, ground soil and sand commonly used in production of sandcrete blocks in the area. The experimental methods used were the titrimetric, gravimetric and instrumental. All the experiments were conducted as specified in [18-22]. The Analyses were carried out to determine the percentage content of SiO_2, CaO, MgO Al_2O_3, Fe_2O_3, Na_2O, and loss on ignition.

RESULTS AND DISCUSSION

Experimental results presented in Tables 1-6 show the percentage compositions of the various cement-based structures. The two ground soil samples gotten from the area in Ung/Muazu Kaduna were found to be humus in nature.

Table 1: Chemical Composition of Sandcrete Samples from Zone I (%)

Compound	Ground soil	Ground level		Middle level		Top level	
		Left side	Right side	Left side	Right side	Left side	Right side
SiO_2	51.76	78.49	78.48	77.0	77.1	76.72	76.8
CaO	1.50	4.04	4.05	5.56	5.55	5.98	5.96
MgO	0.19	0.18	0.18	0.16	0.162	N.D	N.D
Al_2O_3	21.43	3.55	3.53	3.02	3.00	2.98	2.98
Fe_2O_3	8.98	3.09	3.06	2.99	2.97	2.95	2.95
Na_2O	0.75	0.68	0.67	0.77	0.77	0.81	0.80
K_2O	1.82	0.435	0.435	0.423	0.422	0.391	0.393
SO_3	0.01	0.145	0.149	0.151	0.153	0.161	0.161
LOI	13.56	9.44	9.44	9.89	9.83	10.01	10.00
Σ	100.00	100.00	100.00	100.00	100.00	100.00	100.00

Table 2: Chemical Composition of Sandcrete Samples from Zone II (%)

Compound	Ground soil	Ground level		Middle level		Top level	
		Left side	Right side	Left side	Right side	Left side	Right side
SiO_2	49.41	78.5	78.63	78.63	78.7	77.52	77.52
CaO	1.42	4.10	4.09	4.00	4.01	5.49	5.49
MgO	0.20	0.16	0.16	0.15	0.15	0.001	N.D
Al_2O_3	22.91	3.36	3.31	3.08	2.99	2.86	2.85
Fe_2O_3	9.57	2.98	2.98	2.87	2.88	2.73	2.74
Na_2O	0.71	0.68	0.69	0.77	0.77	0.81	0.81
K_2O	1.71	0.423	0.424	0.412	0.411	0.393	0.393
SO_3	0.05	0.151	0.15	0.156	0.155	0.160	0.161
LOI	13.76	9.57	9.56	9.93	9.93	10.04	10.03
Σ	99.74	100.00	100.00	100.00	100.00	100.00	100.00

Table 3: Chemical Composition of Sandcrete Samples from Zone III (%)

Compound	Ground soil	Ground level		Middle level		Top level	
		Left side	Right side	Left side	Right side	Left side	Right side
SiO_2	73.42	80.3	80.3	79.4	79.4	79.3	79.3
CaO	3.08	3.83	3.82	4.25	4.26	4.44	4.44
MgO	0.60	0.17	0.17	0.15	0.14	N.D	0.002
Al_2O_3	6.15	3.02	3.00	3.00	3.01	2.98	2.97
Fe_2O_3	3.99	2.98	2.98	2.94	2.95	2.89	2.88
Na_2O	0.85	0.64	0.65	0.68	068	0.70	0.71
K_2O	1.98	0.425	0.426	0.414	0.414	0.400	0.401
SO_3	1.13	0.153	0.154	0.16	0.16	0.165	0.167
LOI	9.31	8.57	8.44	8.98	8.98	9.13	9.12
Σ	100.51	100.00	100.00	100.00	100.00	100.00	100.00

Table 4: Chemical Composition of Sandcrete Samples from Zone IV (%)

Compound	Ground soil	Ground level		Middle level		Top level	
		Left side	Right side	Left side	Right side	Left side	Right side
SiO_2	72.89	79.67	79.65	79.67	79.64	79.29	79.30
CaO	3.18	3.92	3.92	4.10	4.11	4.35	4.36
MgO	0.62	0.18	0.18	0.16	0.16	0.002	0.001
Al_2O_3	6.24	3.32	3.33	3.23	3.23	3.33	3.31
Fe_2O_3	3.97	2.79	2.79	2.69	2.70	2.61	2.61
Na_2O	0.82	0.71	0.72	0.75	0.75	0.801	0.805
K_2O	1.82	0.35	0.349	0.341	0.342	0.34	0.34
SO_3	0.92	0.154	0.155	0.16	0,16	0.175	0.i73
LOI	9.58	8.89	8.90	8.90	8.91	9.10	9.10
Σ	100.09	100.00	100.00	100.00	100.00	100.00	100.00

Table 5: Chemical Composition of Sandcrete from Uncracked Zone (%)

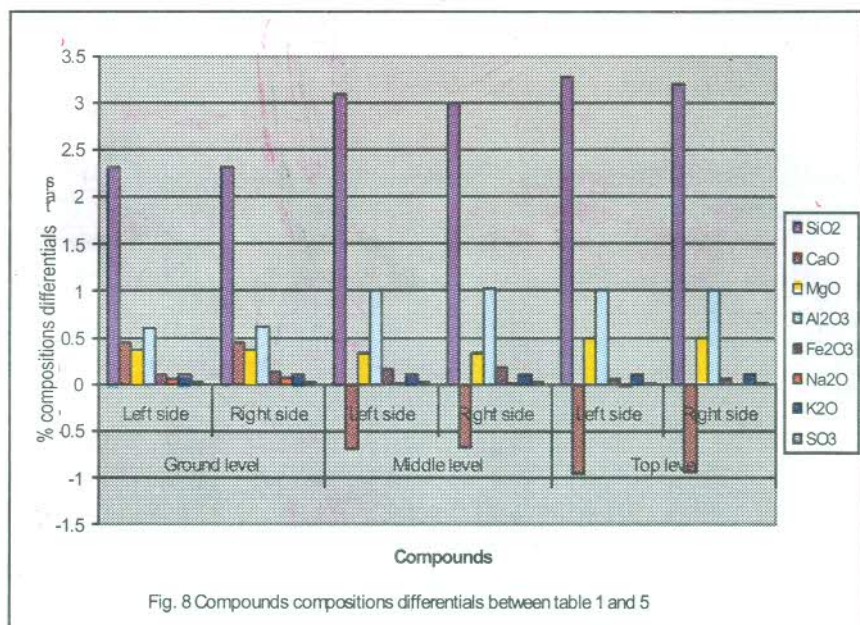| Compound	Ground level	Middle level	Top level
SiO₂	80.80	80.1	80.0
CaO	4.49	4.87	5.02
MgO	0.542	0.501	0.492
Al₂O₃	4.15	4.02	3.98
Fe₂O₃	3.19	3.14	3.00
Na₂O	0.74	0.78	0.80
K₂O	0.54	0.53	0.49
SO₃	0.170	0.172	0.169
LOI	5.38	5.85	6.01
Σ	100.00	100.00	100.00

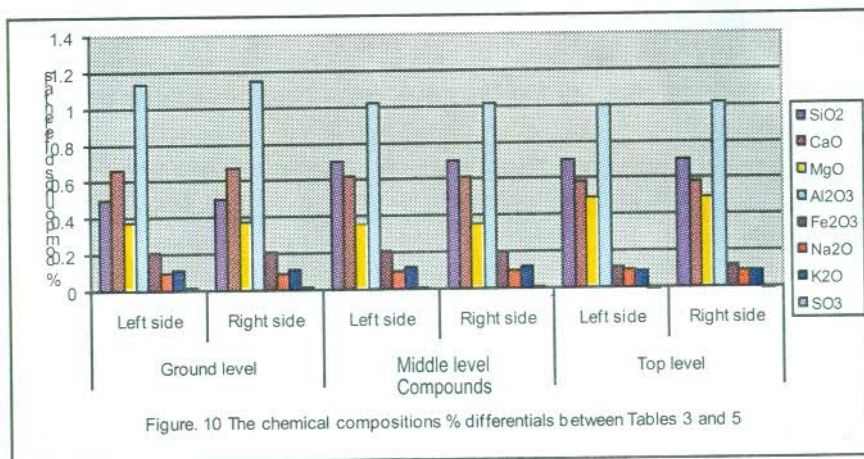Fig. 8 Compounds compositions differentials between table 1 and 5
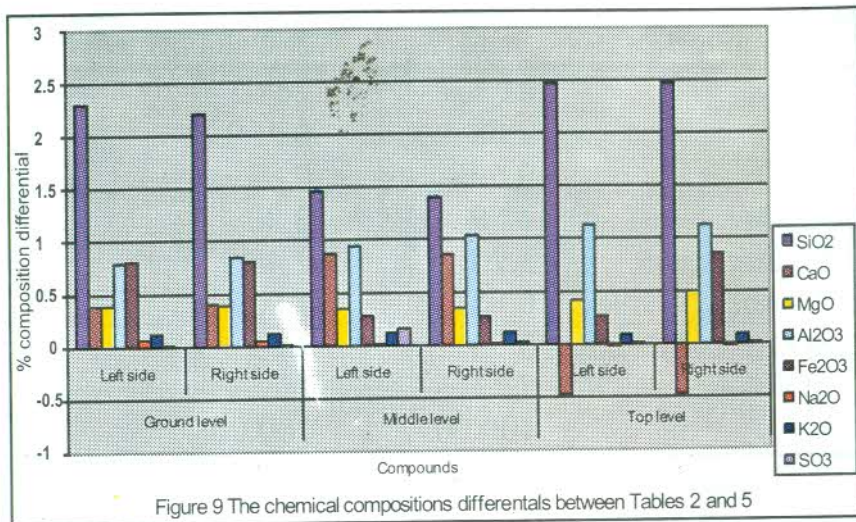
Table 6: Chemical Composition of a Indigenous Cement Brand and Typical Sharp Sand from Kaduna Used Predominantly for Sandcrete Block Production and Mortar.

Compound	Sand, %	Ashaka cement %
SiO_2	81.63	26.03
CaO	1.68	62.00
MgO	0.52	0.82
Al_2O_3	4.89	3.80
Fe_2O_3	3.20	2.40
Alkalis	0.82	1.05
SO_3	0.03	1.65
LOI	7.23	2.25
Σ	100.00	100.00

The sandcretes chemical analyses data presented show that the percentage composition of SiO_2 is relatively high in all the samples varying from 76.72 80.3%. In all the samples the ground levels have the highest SiO_2. This pattern of high SiO_2 concentration at the ground, compared to the upper level is an indication of relatively high permeability of soil water and fresh rainwater solutions into the structure. This pattern is the same even for the control sample.

pH tests carried out on the ground soil (Tables 3 and 4) show that the soil is humus in nature and acidic. In presence of moisture and long exposure of the structure to soil water, the acids could react with cement mineral hydrate especially Ca $(OH)_2$ to produce perhaps soluble calcium salt and water. The leaching of the resultant product from the hardened matrix exposes it to further attack, leaving behind a weak structure. It is also well documented that such pH considerably enhances metal reinforcement corrosion.

Figure 9 The chemical compositions differentals between Tables 2 and 5

Figure. 10 The chemical compositions % differentials between Tables 3 and 5

The data in Figures 8 to 11 show that the alkaline oxides' concentrations (K_2O and Na_2O) were relatively more in the ground levels. In some cases their concentrations at the top level were practically zero. This could be attributed to possible migration of free alkaline hydroxide from the top down especially during the rainy seasons. The high moisture content of exposed cement-

based structure during this period enhances diffusivity and easy leaching of the alkali from the lower level to the ground water and their consequent migration from top down.

From Tables 1 - 4, the percentage content of calcium oxide CaO at the ground level was always the lowest while the top was the highest. It varied from 3.83% for ground level to 5.96% at the top level. This discrepancy could be attributed to the gradual leaching of the mineral hydrates from the structure matrix. The leaching process leaves behind a spongy matrix and enhanced ground water diffusion into the structure[13,18]. The analysis of Figure 8 - 11 shows that comparatively the uncracked wall CaO content was relatively high. The cracking process might also have been enhanced by the poor sand cement ratio used for the production. The cement content or quality could not ensure proper binding of the fine aggregates. Consequently the physico-mechanical properties of the sandcretes produced were very poor.

The percentage composition of Al_2O_3 and Fe_2O_3 generally followed a decreasing order from ground to top level, in almost all the Tables. The ground soil of the sample in Table 1 had an alumina content of 21.43% and ferrous oxide 8.98%. In Table 2 alumina it was 22.91% and ferrous oxide 9.5%. In Table 3 the alumina content was 6.15% while ferrous - 3.97%.
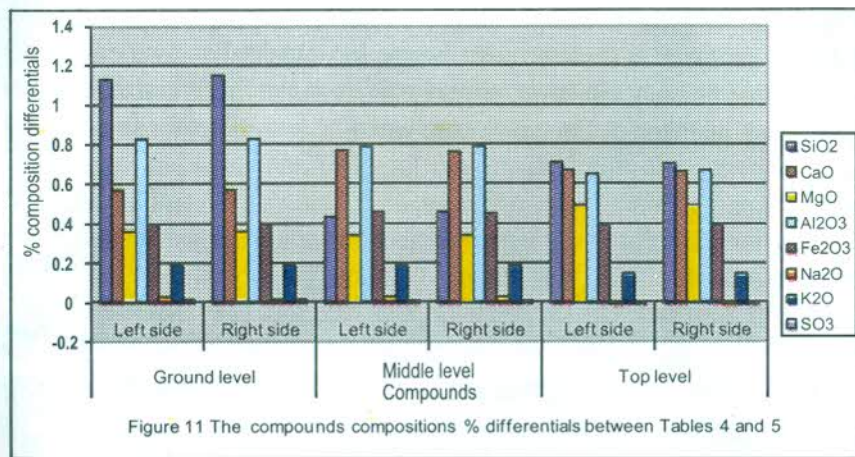

Figure 11 The compounds compositions % differentials between Tables 4 and 5

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The ground soils for Zones 1 and 2 are clayish in nature while those of Zones 3 and 4 were humic. Comparative analyses as presented in Figures 9 to 11 show that the alumina and ferrous contents differ from the standard sample value for the ground, middle, and top levels.

From all the Tables 1 to 4, magnesia (MgO) was found to be about 0.19% with majority of this coming with the sand. Table 6 shows the percentage composition of the cement merges well with type IV and probably I of ASTM and NIS Portland cement[20,21].

The data presented in Table 6 show that the sand percentage composition (SiO_2 is 81.63%, calcium oxide is 1.68%, followed by Al_2O_3 and Fe_2O_3 which are 4.89% and 3.20% respectively) were within limit[22]. The percentage loss on Ignition (LOI) of 7.23% was within acceptable limit for sandcrete blocks production and therefore may not undermine its physico-mechanical properties.

MATHEMATICAL MODELLING OF POLLUTANTS' DIFFUSION INTO SANDCRETE STRUCTURE

Sandcrete structure may have porosity of more than 25% depending on the extent of vibration. The sandcrete block forms the major construction material in Nigeria building industry. Nigeria is a developing country. Pollution problem associated with heavy industrialization is today being experienced globally. However, all mitigating features to combat the trend of event have all failed in the developing world as a result of these countries being converted to dumping ground 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 CO_2, SO_2, Cl^-, CO, NO_x, etc. The presence of these pollutants has contributed not only to the depreciation of the peoples' life quality but also to the degradation of cement based structures physico-chemical, mechanical and aesthetic qualities[9].

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. The rate of the pollutants' diffusion into the matrix will therefore 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.

Basic assumption

The following assumptions were made to facilitate the derivation of the deterministic model equation[23-26].

1.   The cement block is well compacted and therefore available inter pore space is assumed to be spherical.
2.   The 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.

The overall rate of reaction W_A of a component A on the structure was derived as[12]

$$C_A \quad W_A \frac{1}{D_e} lnr \quad \text{or } r_p = W_A = C_A D_e / lnr \qquad 1$$

where W global rate of reaction, lnr natural logarithm of depth of pollutant gas penetration, C_A adsorbed concentration on the solid surface, mole/g, D_e effective diffusivity of the gaseous pollutants, per unit of the total cross sectional area.

This model gives the rate of generation of the reaction product. The values earlier obtained for W_A and D_e are presented in Tables 1 and 2

EXPERIMENT

The samples A (20 years old) and B (15 years old) were collected from

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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 distance into the blocks 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 500km north of Lagos. All samples were assumed to be produced by mixing sand and cement with potable water. The mixture with moisture content of 30 40% is then poured into mould and compressed either manually or vibrated mechanically. Minna is a city with practically no functional large-scale industry, consequently except from automobile 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 6 8% residue on a 80m size mesh. All the chemical analyses were conducted according to standard quantitative analyses techniques.

RESULTS AND DISCUSSION

Results of the experiments are presented in Figures 12 and 13 and Table 7. From equation 1, C_A is directly proportional to the natural logarithm of depth of pollutant penetration, lnr. The gradient of the line so obtained will be equal to W_A/D_C. W_A for a given pollutant is calculated from the quantity of reaction product deposited in the sandcrete over the experimental period.

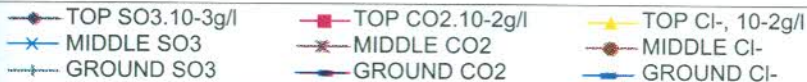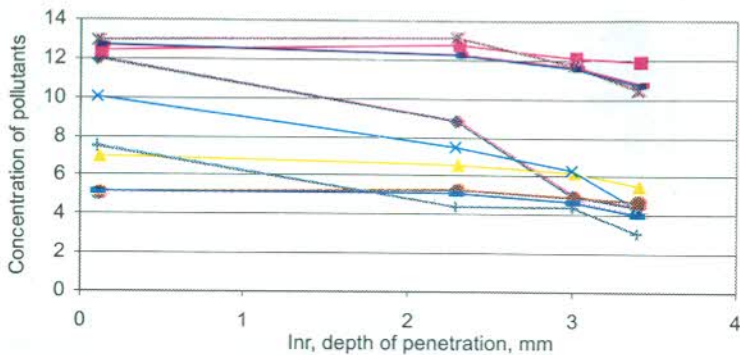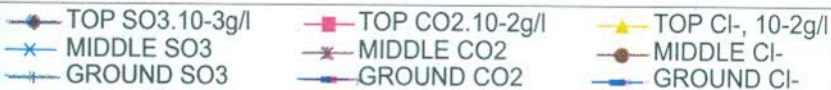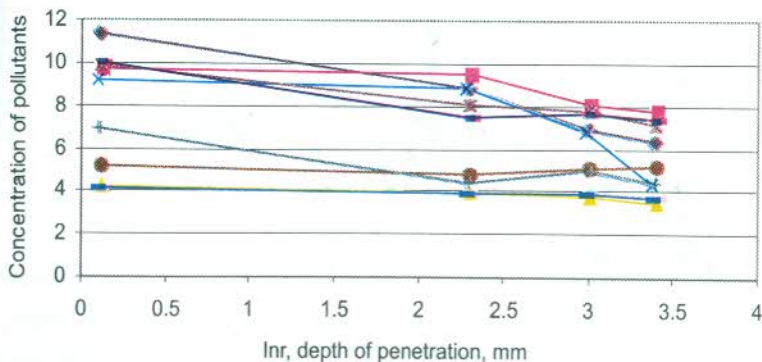Figure 12 Concentration of pollutants versus depth of penetration in site A

Figure 13 Concentration of pollutants versus depth of penetration in site B

The results of analysis of the rate of reaction for the various pollutants are presented in Table 8 and 9.

Table 7 Averaged concentration of $Ca(OH)_2$ at different depths

Depth, r, mm	Samples concentration. 10^{-2} g/l		
	Control	A	B
0.9	9.3	8.0	7.7
10.0	10.4	8.3	7.8
20.0	10.7	8.5	7.9

Table 8 Rate of various pollutants' deposition in sandcrete block

Depth, r, mm	Rate of SO_3 deposition, $.10^{-9}$(g/l)/hr at depths, for samples from sites A and B at different levels					
	Top		Middle		Ground	
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 deposition, $.10^{-8}$(g/l)/hr at depths, for samples from sites A and B						
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^- deposition, $.10^{-8}$(g/l)/hr at depths for samples from sites A and B						
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
30.0	32	45	2.7	40	23	29

Table 9 Diffusivities coefficients of pollutants in samples at different depths and levels

Depth, mm	Diffusivity of SO_3, $.10^{-6}$ mm/hr at depths, for samples from sites A and B					
	Top		Middle		Ground	
	A	B	A	B	A	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
CO_2						
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
Cl						
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

Show equilibrium or reverse in the relative rate of products deposition in the sandcrete depths. This retards the diffusivity of the pollutants.

The CO_2, SO_2 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 (SO_2, CO_2 and Cl) were dependent on the level and depth of sampling (Figures 12 and 13 and Table 8). The concentration of and Cl in the block increased by 3 - 10.5 and 1- 2 times respectively over a 15 - 20 years period. The significant disparity in the concentration maybe connected to the conversion of the insoluble $CaCO_3$ to soluble $Ca(HCO_3)$ and its subsequent leaching. The concentration of SO_3 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; with only about 60% extent of hydration attained after 180 days even for fast hydrating cement. The free $Ca(OH)_2$ is continuously utilized through various reactions such as in 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 presence of active SiO_2, $Ca(OH)_2$ will reactive to produce various solid solution of C-S-H.

The porous nature of sandcrete block ensures that the increased volume experienced as increased stress during the formation of ettringite in the course of the reaction involving $CaSO_4.2H_2O$ and calcium aluminate/ferrite hydrates is completely adsorbed. Unlike SO_2 pollutant and sometimes CO_2, Cl^- will always lead to increased porosity of the structure as the resultant soluble $CaCl_2$ or unstable monochloroaluminates can be easily removed via leaching.

Analysis of Table 8 showed that the rate 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 was fairly well distributed in all the depth 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 variation for Cl^- was the least. The difference in the various rates of reactions involving SO_2, Cl_2 and CO_2 for samples A and B, showed that the observed $Ca(OH)_2$ content could not have been the products of the primary reactions of cement minerals hydration[17,27]. Their continuous presence is the resultant of various secondary reactions involving the cement minerals' hydrates and pollutants introduced into the sandcrete block.

The outer layer diffusivity values, for all the pollutants investigated were for most cases, higher than those of the interior (Table 9). However, the observed disparities of D values between layers' depth might be connected with the non-uniform 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 CO_2 was enhanced by its relative abundance in the atmosphere. The deposition of $CaCO_3$ on the outer surface of sandcrete block reduces the penetration of CO_2 into the structure. The non uniformity 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 $CaCO_3$ to $Ca(HCO_3)_2$ 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 observed result is very critical in forecasting the probability of structure failure/collapse. The effect of these pollutants in solution as in cases of flooding of building or exposure of foundation to such solution could be catastrophic. This might be a contributory factor in some collapsed of high rise building in Lagos and very recently in Haiti.

Mathematical modelling of pollutants' diffusion into sandcrete structure
The schematic diagram of the structure is presented in Figure 14. The driving forces of the deterioration (weathering) process are the physical and chemical reactions. It is well established that two principal conditions must be meet for this process to proceed; 1. The compounds are present as mineralized water soluble form and 2 the environment where dispersion occurs is water saturated.
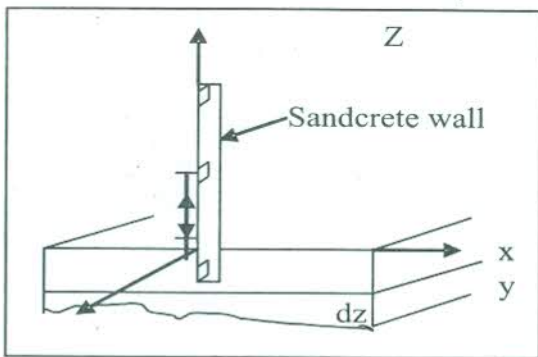
Figure 14 Schematic diagram of sandcrete wall and an exposed 1 year old sandcrete block

In developing a model for dissolved hydrates migration towards the ground level in sandcrete wall various dispersion models[26-32] were considered.

Let's consider the distribution of the reaction products across the wall and relative to the ground level. It will be assumed that the reaction products on dissolution do not react with the neighboring "healthy" hydrates and can only be leached downwards. That is the reaction is not sensitive to r and z. The reaction condition is isothermal and the velocity is not a function of z. Therefore

$$u \frac{C}{z} \quad D_{e\ L} \frac{^2C}{z^2} \quad r_p \quad 0 \qquad\qquad 2$$

Equation 2 expresses the global rate of formation of the reaction product on

the sandcrete surface $r_p =$, $\dfrac{C_A D_e}{Inr}$ rate of dissolution $D_{e\ L} \dfrac{^2C}{z^2}$

and migration to the ground level $u\dfrac{C}{z}$.

The quantity of dissolved salts dM_A displaced per unit time t across a unit area $y\ z$ at a randomly chosen point on the x axis can be represented as

$\dfrac{dC_A}{dx}$. That is the amount is directly proportional to the concentration

gradient, size of the unit, time and inversely proportional to the viscosity of the medium μ.

Therefore equation 2 can be presented as

$$u\frac{C}{z}\quad D_{e\ L}\frac{{}^2C}{z^2}\quad \frac{C_AD_e}{Inr}\quad 0$$

$$3$$

$$\frac{{}^2C}{z^2}\quad \frac{u}{D_{e\ L}}\frac{C}{z}\quad \frac{D_e}{D_{e\ L}Inr}C_A\quad 0$$

This is equivalent to a quadratic equation $k^2\ pk\ q=0.\ P=\dfrac{u}{D_{e\ L}}$ and

$q=\dfrac{D_e}{D_{e\ L}Inr}$

The solution to a quadratic equation can be represented as

$$k\quad \frac{b\ \sqrt{b^2\ 4ac}}{2a}\quad \frac{\dfrac{u}{D_{e\ L}}\ \sqrt{\left(\dfrac{u}{D_{e\ L}}\right)^2\ 4\dfrac{D_e}{D_{e\ L}Inr}}}{2}\quad 4$$

u = z/t = where z = 0.01, 0.75 and 1.5m and t = 15 and 20 years.

In equation 3, $(D_e)_L$ which is the effective diffusivity of the ions in the concrete medium is the unknown parameter. However it can be, for very close interval, approximately determined from the gradient. D_e is the effective diffusivity of

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the gas into the structure and the calculated values are presented in Table 9, r = 0.9 30mm.

The ratio $D_e/(D_e)_L$ defines the extent of reaction between the cement mineral hydrates with the pollutants and their denudation (leaching) from the structure.

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 distance into the blocks wall used for the fence; at the top (1.5m), middle (0.75m) and ground (0.01m) levels. The control sample (1 day old) was collected from a block industry in Minna; about 500km 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 mould and compressed either manually or vibrated mechanically. Minna is a city with practically no functional large-scale industry, consequently except from automobile and the homes not many pollutants are generated. Each of the collected samples were ground in a ceramic lined mill to a fineness of about 6 8% residue on a 80m size mesh. The compressive strengths of sandcrete blocks produced from various parts of Nigeria for 450 mm x 225 mm x 225 mm and 450 mm x 150 mm x 225 mm blocks vary 0.11-0.45 N/mm^2 and 0.11-0.55 N/mm^2 respectively.

Analysis of results obtained showed that the rate of deposition of all the pollutants investigated is higher at the outer surface. There is an inverse proportionality relationship between the rate of reaction and the natural logarithm depth of the pollutants' penetration. The outer layer diffusivity values, for all the pollutants investigated were for most cases, higher than those of the interior. The calculated diffusivity values as represented in Figures 15 and 16 indicate a sinusoidal relationship with depth. There is the

possibility that there is a phase change with time comparing the two figures.

Figure 15 Calculated diffusivities for sample A

Figure 16 Calculated diffusivities for sample B
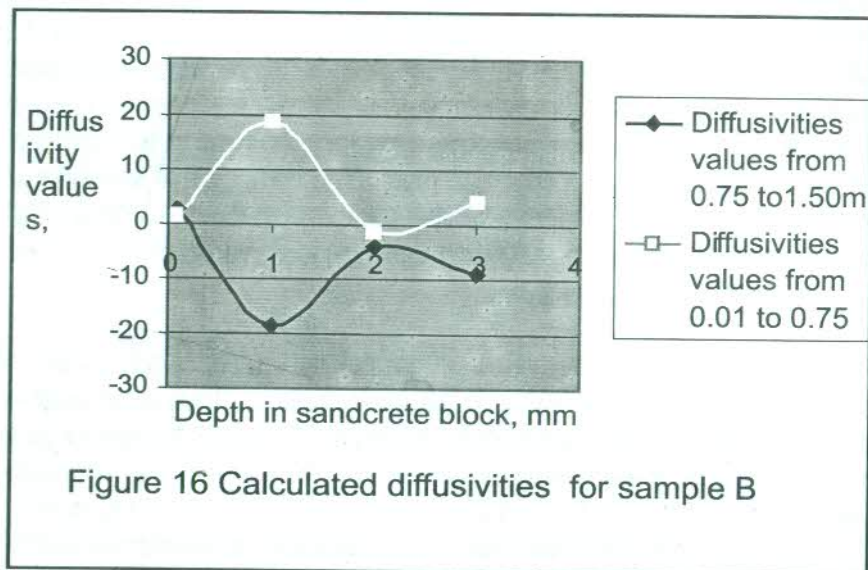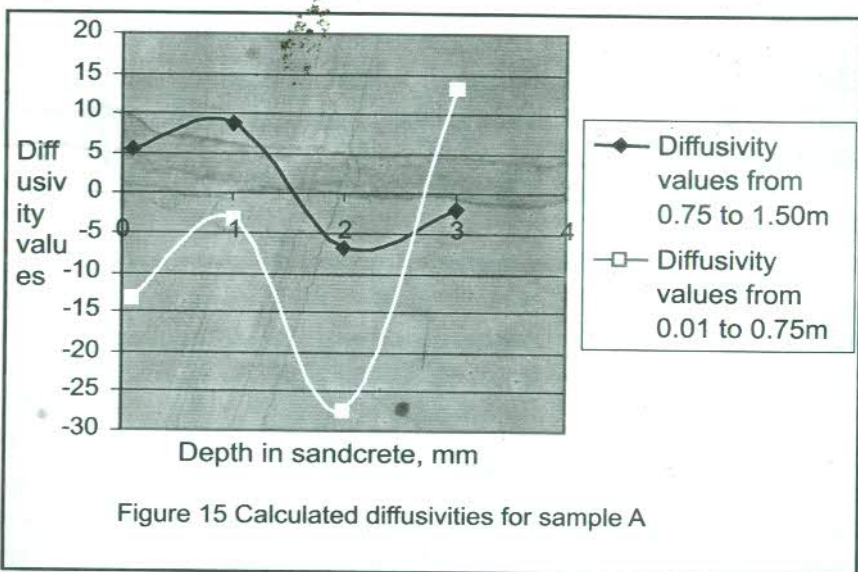
The diffusivity D_e represents the actual value of CO_2 molecules that diffuse into and reacted with the cement minerals. It can not be negative (-) but does vary in the structure volume. $(D_e)_L$ represents the dispersion of the dissolved $CaCO_3$ as $Ca(HCO_3)_2$ in the volume. From the region of high to lower concentration (the reverse may be possible) in presence of water. Analysis indicates that the carbonate concentrations in the ground level remain higher compared to the middle and upper levels especially for the outer layer[33]. In the inner layers the reverse seems to be true.

The equations that best represent the integrated solutions to equation 3 at the ground level (below 0.75) in various depths are for samples A and B are

$$C_A \quad 1.65x10^{4} Sin0.121ze^{0.065z}$$ at depth of below 0.9mm

$$C_B \quad 1.98x10^{4} Sin0.126ze^{0.219z}$$

$$C_A \quad 3.28x10^{4} Sin0.061ze^{0.008z}$$ at depth of below 2 mm

$$C_B \quad 2.64x10^{4} Sin0.378ze^{0.219z}$$

Similarly equation can be obtained for various locations along the sandcrete wall. The graphs of $C = f(z)$ are presented in Figure 17.

Knowing the initial maximum possible carbonation value, which represents the leachable $Ca(OH)_2$ concentration, the derived model equations could be used to predict the cement minerals depletion rate from the structure. Analysis of Figure 17 using their concentration gradient clearly indicates a higher concentration depletion rate at the surface level. The variations between the surface and the inner levels were 1.5 - 1.87 and 2.5 times for sample A and B respectively.

Figure 17 Simulated carbonate concentration for samples A and B at various wall height
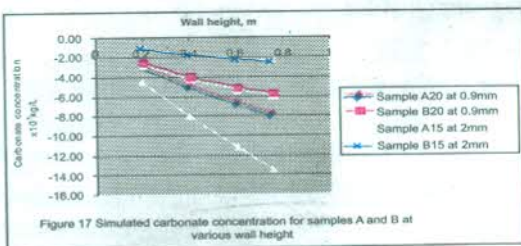
Deterioration mechanism in serving structure could therefore be considered to depend on the:

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.

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.

In general the study showed that the overall pollutants' D values in 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 serving sandcrete block. The higher the diffusivity, the lesser will be the expected mechanical strength of the structure. Thos is an interesting area we shall be developing soonest.

The Nigerian Cement Brands

One of the essential byproduct of the iron and steel industry is the slag. Depending on the production technology, metallurgical slag can be classified into open hearth, convertor and arc types or into basic and acidic based on the chemical compositions. Apart from the $CaO:SiO_2$ ratio that determined its acidity or basicity, metallurgical slag may also contain numerous microelements (V, Ni, Cr, Sr, etc.). These microelements greatly influence the kinetic of the molten solution crystallization and solidification.

The phase composition of slag varies from one industry to another. It is determined by the chemical composition of the initial raw mix and regime of cooling. In metallurgical slag the formations of numerous crystalline phases have been fixed[34]. Molten slag is a heterogeneous ionic liquid, consisting of oxides of cations (Na, Mg, Ca, etc.) and complex anions in the form of $Si_xO_y^{2-}$.

The presence of alkaline earth metals, TiO_2, CrO_2, etc. can significantly regulate the extent of polymerization of the anionic silicate complex. Typical chemical compositions of some slag are presented in Table 10. It clearly showed that the chemical compositions of some slag resemble that of cement clinker.

Table 10: Typical chemical composition of Iron/Steel Industry Slag

Country	Source of slag	Chemical composition, mass %									
		SiO_2	Al_2O_3	Fe_2O_3	FeO	CaO	MgO	MnO	SO_3	S	Total
Russia	Shaft furnace	22.74	1.48	2.95	12.36	39.07	12.28	8.52	0.62	0.23	100.25
	Convertor	28.23	2.54	2.08	7.78	42.32	7.38	7.53	1.82	0.67	100.38
UK	Shaft furnace	7.00			20.00	50.55	1.00-1.50	3.00			
	Convertor	10.00-15.00	1.50-2.50		5.00-15.00	50.00-55.00	5-10	3.00-5.00			
USA	Shaft furnace	15.30	0.60		17.80	41.60	11.80	4.00		0.90	92.00
	Convertor	51.80	3.30		23.90	5.10	0.12	11.30			95.52
Cement		21.00-24.00	4.00-8.00	2.00-4.00		63.00-66.00					

The mineralogical composition of metallurgical slag is dependent on the technology of pig/steel production, most especially the rate of cooling of the molten slag. However it is generally agreed that the mineralogical composition be regulated to closely resemble that of cement clinker.

Based on the resemblance in chemical and mineralogical compositions, metallurgical slag is widely used in the cement industry; first, as additive in the production of slag Portland cement and second, as raw mix component mainly in partial substitution of $CaCO_3$ and Fe_2O_3. The former utilization of slag is most favoured.

Metallurgical Slag in Production of Slag Portland Cement

Cement production is an energy intensive business. About 7000KJ of fuel and 30kW/h of electricity are required to produce l kg of cement clinker. The electroenergy and fuel demands contribute about 13 and 25% to the cement production cost. The energy cost required for the production of 1 kg of pig iron is also in the neighborhood of above 30%. For an optimized pig iron raw mix composition the volume of slag produced range between 30 to 60%.

There is the need to ensure proper utilization of the huge amount of energy expended in the production of these products and contained in the outgoing byproducts. This has necessitated the production of a cement blend called slag Portland cement. It has been documented that with proper optimization of raw mix and cooling regime of metallurgical slag, the chemical and mineralogical compositions will be equivalent to that of cement clinker. Such slag can substitute up to 90% of Portland cement clinker. Slag Portland cement is known to possess specific characteristics that make it very suitable for general use and special applications. The use of ground granulated blast furnace slag enhances plastic properties of short and long term durability and is environmentally beneficial. Researches have also proved that even with lean slag, the inclusion of certain additives can influence its rate of hydration[27]. Various technologies of slag and slag Portland cement productions have been developed patented and are currently used in the developed economy. It is important to note that even some of the imported cement to Nigeria maybe slag Portland cement. The complexity of each technology is dependent on the chemical/mineralogical properties of the slag.

In the cement industry, byproducts such as slag, flyash, etc. are being used as additives in partial substitution of $CaCO_3$, Fe_2O_3 and Al_2O_3 or as fluxes with the aims of reducing the moisture content[35,36], sintering temperature[37], increasing the reactivity of the raw mix components and cement produced[38]. It is well established that the introduction of some byproducts containing microelements capable of positively influencing the sintering process, remains the most prospective direction for intensification of cement production process.

Despite the economic advantages to be derived from introduction of slag to cement raw mix its application in cement technology is still very limited. The wider application is hindered by many difficulties. Metallurgy slag contains about 6% metallic iron, even when extracted and ground, the resultant powder may contain between 1 - 2% metallic particles and more than 10% iron oxides. Utilization of slag has resulted in sedimentation or settling of

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cement raw mix. During sintering it is claimed that the introduction of slag may increase the retention time of clinker minerals formation process, but will reduce the overall clinkerization temperature. Complete adsorption of CaO in slag during clinkerization takes place at higher temperature ($30 - 50°$ higher than that of CaO from natural mix[39]). Various technologies have been developed to tackle these problems[40,41]. However these technologies are slag specific and greatly dependent on the established raw mix composition[42-50].

CASE STUDIES
Presented below are the results of my 2 patents based on the utilization of open hearth furnace slag; first for the production of slag Portland cement and second as raw mix for the production of cement clinker. Also presented are the results of some Portland cement brands commonly sold in the Nigerian market.

Patent 1 Technology of Aggregate Preparation for Concrete Mix[42]
The patented technology is directed at increasing the bonding of aggregates to cement hydrates. The aggregates are acidic open-hearth slag and coarse sand. The slag is treated with a paint industry byproduct at a given temperature and time followed by a dilute solution of an acid and the entire mixture is then dried. The treated slag is now ready for use as aggregate for concrete production. The experimental result of this technology application is presented in Table 11.

Table 11: Compressive strength of Concrete mix

S No	Composition of concrete, mass %			Compressive strength of Samples, MPa, after days		
	Treated slag	Cement	Sand	7	28	90
1	15.0	17.5	67.50	25.7	45.0	53.0
2	15.0	17.5	67.50	30.0	30.0	53.5
3	17.5	16.25	66.75	30.5	43.5	52.0
4	15.0	17.5	67.50	25.0	46.0	53.0
5	15.0	17.5	67.50	30.2	36.0	53.5
6	17.5	16.50	66.75	31.5	44.5	53.0

Patent 2. Slag as Raw Mix for Cement Clinker Production[43]

The main aim of the patent was to increase the compressive strength of cement clinker and reduce its sintering temperature via the utilization of by-products containing microelements. In this patent the use of open-hearth slag and abrasive slurry from machine building industry were found, after proper optimization of the raw mix, to enhance the rate of decarbonization and reduce the liquification temperature (Tables 12- 13).

Table 12 Chemical Compositions of Raw Materials

Material	Oxides content, mass %								
	SiO_2	Al_2O_3	Fe_2O_3	FeO	Fe	CaO	Cr_2O_3	MnO	LOI
Limestone	7.66	1.19	0.62			49.50			39.95
Sand	76.71	6.60	2.81			6.64			5.61
Open hearth slag	37.17	11.05	14.56			20.72	3.57	9.32	
Abrasive slurry 32°C									
*1400°C	3.02	27.00	4.34	6.72	54.00	0.84	1.82	0.6	
*500°C	1.10	22.54	74.24		1.10				
	1.32	16.42	60.52	9.5	10.3			1.31	

Expected chemical composition of abrasive slurry burnt at 500 and 1400°C. LOI - Loss on ignition.

Table 13 Composition of Raw Mix and Compressive Strength of Cement

N	Composition of raw mix, mass %				Compressive strength MPa, after, days		
	Limestone	Open hearth slag	Abrasive slurry	Sand	7	28	180
1	82.00	5.00	4.00	9.00	37.0	40.1	52.5
2	79.00	7.00	5.00	9.00	25.0	37.7	46.7
3	80.00	8.00	3.00	9.00	28.5	34.5	52.5
4	80.33	6.34	4.33	9.00	26.5	36.4	46.0
5	79.67	6.66	4.67	9.00	34.0	43.5	52.5
6	79.25	7.30	4.40	9.00	19.0	35.0	49.1
7	79.53	7.80	3.67	9.00	34.0	48.2	61.9
8	81.03	6.67	3.30	9.00	40.0	34.4	59.9
9	79.73	7.60	3.67	9.00	32.0	42.6	53.7
10	80.03	6.67	4.30	9.00	23.0	37.7	49.1

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Abrasive slurry 32°C									
*1400°C	3.02	27.00	4.34	6.72	54.00	0.84	1.82	0.6	
*500°C	1.10	22.54	74.24		1.10				
	1.32	16.42	60.52	9.5	10.3			1.31	

Expected chemical composition of abrasive slurry burnt at 500 and 1400°C. LOI - Loss on ignition.

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2	79.00	7.00	5.00	9.00	25.0	37.7	46.7
3	80.00	8.00	3.00	9.00	28.5	34.5	52.5
4	80.33	6.34	4.33	9.00	26.5	36.4	46.0
5	79.67	6.66	4.67	9.00	34.0	43.5	52.5
6	79.25	7.30	4.40	9.00	19.0	35.0	49.1
7	79.53	7.80	3.67	9.00	34.0	48.2	61.9
8	81.03	6.67	3.30	9.00	40.0	34.4	59.9
9	79.73	7.60	3.67	9.00	32.0	42.6	53.7
10	80.03	6.67	4.30	9.00	23.0	37.7	49.1

Conclusion
Where we are
Cement sold in the Nigerian market is commonly referred to as Portland cement. By International standards its chemical composition is well defined and standardized. Most analyses conducted in Nigeria are based on comparative analysis of the experimental and standard values. Their reliability is superficial and can not be dependable in assessing the suitability of cement for all service conditions. Cement should be designed and produced with a desired utility specification.

Nigerian sandcrete
Cement-based sandcrete block is the main building object in Nigeria. It is as historical as the building industry and the most preferred. The following deductions could be made from our research about sandcrete: The observed rate of CO_2 sequestration by sandcrete structure in the most industrialized city in Nigeria is about $7.0x10^{-7}$(g/l)/hr or 0.7kg/ton.hr. It also has the ability to sequestrate chloride (about 0.3kg/ton.hr) and sulphate (about 0.6kg/ton.hr) from the atmosphere and solution. Its physico-mechanical and chemical properties can not be defined; it is raw material specific. It is however chemically very active. It is often not designed.

This is a double edged sword conclusion. The first is the potential positive contribution of cement-based structure towards finding a solution to the global warming phenomena. The second is the potential danger of building collapse due to the acidulation of the structure.

Structural failure when expressed as top event - collapsed building is not solely due to reasons generally given expressions to by most investigators. Collapsed building could be associated with the chemistry of the material used and in particular cement chemistry and morphology on the one hand and its interaction with the immediate surrounding on the other including the metal cement interphase.

Blended Portland cement should be standardized and sold with clear

indication of service environment. There is nothing wrong with blended Portland cement. It is an energy-saving and economic binding material, however a designer must be provided the requisite data to ensure service conditioned design of the cement-based structure.

There is the need to define the nature of cement relative to the service environment. With increasing local production capacity, the cement industry should be able to design and produce tailored cement for a given project.

As we move to project defined, client specified cement industry tailored cement our dream for a greener world and sustainable cement-based structure will become a reality.

New design for sandcrete block

The chemistry of deterioration of indicates the eroding of our tradition sandcrete block surfaces. The consequence is more porosity and reduced strength. Our sandcrete block tends to be thermodynamically unstable in their service environment. Our built structure becomes increasingly unstable with age. There is the need to prepare for disaster as most existing buildings particularly in the Northern Nigeria were built with little understanding of cement process chemistry. Solid sandcrete block is better conditioned to resist corrosion than hollow ones. However they possess very poor heat conduction properties.

There is the need to develop new eco friendly sandcrete block based on the following criteria: cost, environmental or service condition, existing technology, etc. There is also the need to reconsider our foundation design standards. We are in the position to think and develop policies and standards on building materials and building along these concepts. This is my proposal.

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Note