CHEMICAL HYDRATION BY ACID LEACHING OF A BRAND OF CEMENT IN NIGERIAN MARKET

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ABSTRACT

In this work, experiment on chemical hydration by acid leaching from a brand of cement in Nigerian market has been studied. The physico-chemical characterization of the sample by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) and X-ray diffraction (XRD) has been examined. The influence of acid concentration and system temperature on the dissolution rates has been investigated. The dissolution rates are greatly influenced by acid concentration and reaction temperature. The dissolution investigations gave rise to activation energy value of 26.3 kJ/mol, which affirmed the diffusion reaction mechanism. Also, about 4.13 s^{-1} and 0.98 were obtained as the system's Arrhenius constant and reaction order for the dissolution process, respectively.

Key words: Cement, Hydration, Leaching, Dissolution kinetics, Hydrochloric acid.
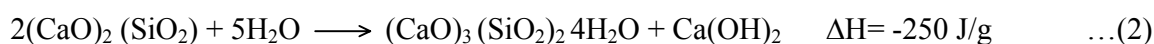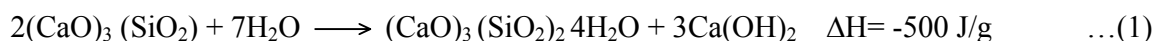
INTRODUCTION

Cement is a binder that sets and hardens independently and binds other materials together. Portland cement is the most common type of cement in general use around the world, because it is a basic ingredient of concrete, mortar, stucco and most non-specialty grout. Cement is a mixture of compound made by burning limestone and clay at very high temperature ranging from 1400-1600°C in a kiln[1].

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A typical cement clinker is a hydraulic material consisting of at least two-third of mass of calcium silicates ($3CaO.SiO_2$ and $2CaO.SiO_2$). Other components consist of aluminum and iron-containing clinker phases and other compounds. The ratio of CaO to SiO_2 shall not be less than 2.0 and the magnesium content (MgO) shall not exceed 5.0% by mass. Gypsum or anhydride is added to the cement clinker in order to achieve the desired setting qualities in the finished product[2].

Cement manufacture can cause environmental impact at all stages of the process. This includes emission of air-borne pollution in the form of dust, gases, noise and vibration when operating machinery, consumption of large qualities of fuel and releases of CO_2 during manufacture[3]. But the cement kiln dust and calcium carbonate generated from the cement manufacture can be converted to both physical and chemical content suitable for recycling in the cement making process (that is, it can serve as secondary raw materials)[4]. Cement is useful in the production of concrete, mortars and grouts.
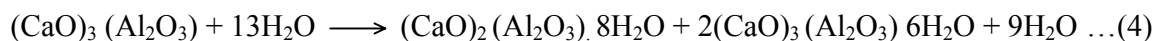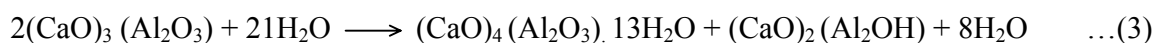
Cement hydration is a chemical reaction in which the major compound form chemical bond with water molecules and become hydrates or hydration products. Both silicate phases (C_2S and C_3S) react with water as shown in the following equations to form calcium hydroxide and rigid calcium silicate hydrate gel:

$$2(CaO)_3\,(SiO_2) + 7H_2O \longrightarrow (CaO)_3\,(SiO_2)_2\,4H_2O + 3Ca(OH)_2 \quad \Delta H = -500 \text{ J/g} \qquad \ldots(1)$$

$$2(CaO)_2\,(SiO_2) + 5H_2O \longrightarrow (CaO)_3\,(SiO_2)_2\,4H_2O + Ca(OH)_2 \quad \Delta H = -250 \text{ J/g} \qquad \ldots(2)$$

Two primary mechanisms of cement dissolution by hydration are:

(i) Through solution: This involves dissolution of anhydrous in solution and eventual precipitation due to their low solubility.

(ii) Topochemical or solid state hydration: Reaction takes place directly at the surface of the anhydrous cement compound without going into solution[5].

Thus, the C_3A reacts with water to form two intermediate hexagonal phases:

$$2(CaO)_3\,(Al_2O_3) + 21H_2O \longrightarrow (CaO)_4\,(Al_2O_3)\,13H_2O + (CaO)_2\,(Al_2OH) + 8H_2O \qquad \ldots(3)$$

$$(CaO)_3\,(Al_2O_3) + 13H_2O \longrightarrow (CaO)_2\,(Al_2O_3)\,8H_2O + 2(CaO)_3\,(Al_2O_3)\,6H_2O + 9H_2O \ldots(4)$$

In the presence of gypsum, tricalciumaluminate (C_3A) form enttringite according to the reaction:

$$2(CaO)_3 (Al_2O_3) + 3CaSO_4.2H_2O + 26H_2O \longrightarrow (CaO)_3 (Al_2O_3) (CaSO_4)_3 \; 32H_2O \quad …(5)$$
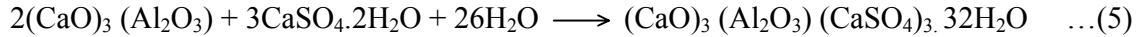
Popular model for describing hydration during acceleration period is the Arrami model of the form:

$$\ln (1-\alpha) = K \, [(t-t_o)]^m \qquad\qquad …(6)$$

Furthermore, Arrami model can also determine the activation energy for the reaction which can be used to access temperature dependence of the reaction and it is expressed as:

$$K(T) = A \, \exp^{Ea/RT} \qquad\qquad …(7)$$

or when α is small,

$$\alpha = Kt^m \qquad\qquad …(8)$$

Where α is the dissolution or degree of hydration, t is time of hydration, t_o corresponds to the length of inductive period and K is a rate constant for a nucleation – controlled process.

From equation (6) and when modeling as a function of time rather than degree of hydration, the following reaction takes place:

$$d\alpha = AmK^m (t-t_o)^{m-1} \exp\{-[k(t-t_o)]^m\} \, dt \qquad\qquad …(9)$$

where A is a pre-exponential factor[6].

Therefore, before hydration occurs, cement paste behaves like a Bingham fluid which yield values between 500 and 1000Pa[7]. Explanations for this early strength include gypsum crystallization, increase of specific surface of ettringite as well as other antiparticle interactions[8,9].

Hence, chemical shrinkage should be sub-divided into dissolution shrinkage and hydration shrinkage. The latter takes place before as well as after the induction period. As expected, the volume of dissolved cement is a function of w/c (Water-to-Cement) ratio, whereas the volume of early hydrated cement is independent of w/c ratio[8]. Therefore, this work was aimed at evaluating the dissolution efficiency of indigenous cement available in Nigerian market by hydrochloric acid leaching. The data obtained will be fitted into suitable kinetic models.

EXPERIMENTAL

Materials and methods

Collection of sample

The sample used for this work was Burham Portland Cement MIS-150, a brand of cement in Nigerian market. It was sourced from Tanke Area, Ilorin, Kwara State, Nigeria.

Reagents

The reagents used for this work are of good analytical grade (BDH product). Concentrated HCl acid was used as the leachant and doubly distilled water was also used in the preparation of all aqueous solutions in this study.

Leaching procedure

Leaching experiment was carried out in 250 mL glass reactor equipped with stirrer. For each leaching experiment, various concentrations of HCl were prepared (0.1 M-1.0 M). The solution was freshly prepared in each case. A 10 g/L of the cement sample was dissolved in 100 mL of 0.1 M HCl and heated to a temperature of $55^{o}C$ at various time intervals (i.e 5, 10, 30, 60, 120 minutes, respectively). At each equilibrium leaching time, the solution was allowed to cool and then filtered through Whattman filter paper. The residue was allowed to dry and also oven-dried at $60^{o}C$ and was weighed afterward. The result of weighed residue was used for calculation of the degree of dissolution hydration. The degree of hydration (α) was evaluated from the initial differences in mass (m_i) amount dissolved or undissolved (m_f) at different leaching time interval after oven-drying at $60^{o}C$. This procedure was repeated for other concentrations of HCl (0.2-1.0 M). The concentration which gave the highest percentage of dissolution (1 M) was used for optimization of other parameters such as particle size and stirring speed. The order of reaction and the activation energy was estimated from the arrhenius plot[10,11].

RESULTS AND DISCUSSION

Result of elemental composition of Burham cement by ICP-MS and X-ray diffracto-metry

Result of elemental composition of Burham cement by ICP-MS

The elemental analysis of the cement by ICP-MS techniques is summarized in Table 1.

Table 1: Result of elemental composition by ICP-MS

Element	Ca	Si	Mg	Al	Fe	Mn	Ni	Mo	Sb	Pb	Nb	Ti	Total
Concent-ration	58.39	21.14	3.78	2.49	0.09	0.0113	0.0185	0.0113	0.0014	0.0005	0.0005	0.0005	85.93

Oxygen = 14.07 obtainable by difference

From Table 1, it is evident that the major elements detected by ICP-MS are Ca, Si, Mg and Al. Other elements ranging from minor to trace levels are Fe, Mn, Ni, Mo, Sb, Pb, Nb and Ti.

Result of phase study by XRD

The result of the sample purity by XRD is presented in Fig. 1.
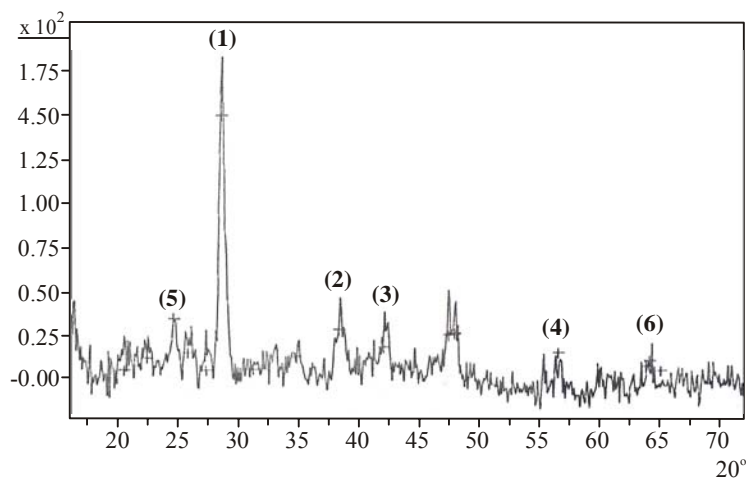
Fig. 1: The XRD spectra of Burham cement showing the most important compounds identified

(1) $(CaO)_3.SiO_2$ {27-0088}, (2) $MgO_2.SiO_2$ {08-0479}, (3) $(CaO)_3 Al_2O_3$ {10-0188}, (4) $(CaO)_4.Al_2O_3 Fe_2O_3$ {25-0127}, (5) $CaSO_4.2H_2O$ {23-0125}, (6) $CaO_2.SiO_2$ {04-0767}. Joint Committee on Powder Diffraction Standards (JCPDS) File numbers responsible for peaks attribution are in curl brackets.

It is evident that the cement under study consist of the following compounds: $(CaO)_3.SiO_2$ (Tricalcium silicate), $MgO_2.SiO_2.$(Magnesium oxide silicate), $(CaO)_3 Al_2O_3$ (Tricalciuminaluminate), $(CaO)_4.Al_2O_3$ (Calcium oxide aluminate). Fe_2O_3 (tetracal-

ciumaluminoferrite), $CaSO_4.2H_2O$ (Gypsum) and $CaO_2.SiO_2$ (Dicalciumsilicate). The result of the XRD compliment the elemental composition by ICP-MS as previously discussed.

Result of leaching investigations

Effect of HCl concentration

The effect of HCl concentration on the rate of cement sample dissolved was examined. The result of fraction of the cement sample dissolved was plotted against the contact time at various concentrations of HCl as shown in Fig. 2.
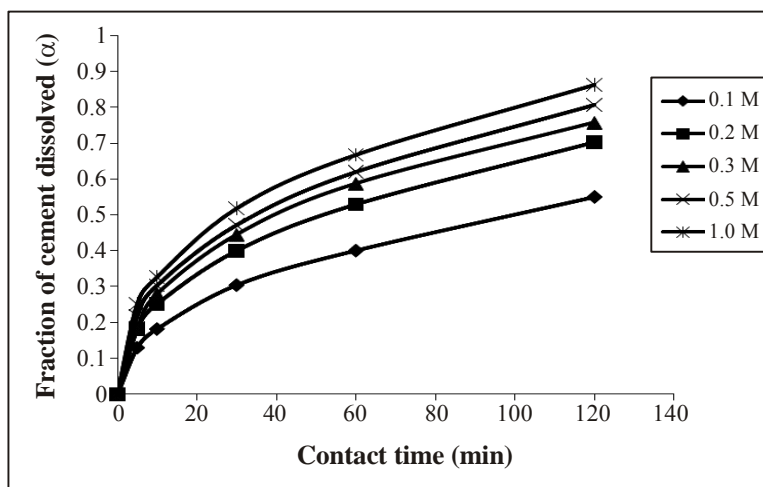

Fig. 2: Plot of fraction of cement dissolved vs contact time at different HCl concentration

Experimental conditions: HCl concentration = 0.1-1.0 M, Temperature = 55°C, Stirring speed = 200 rpm, Particle size = ≤ 0.1 mm.

From the plot in Fig. 2, it shows that an increase in concentration of HCl is accompanied by increase in the amount of cement hydration dissolution at various time intervals up to 120 minutes. Therefore, concentration of the leachant has a significant effect on the leaching of cement sample. Therefore, this result showed that the rate of the cement dissolution is controlled by hydrogen ion concentration.

Effect of temperature

The effect of temperature on the rate of dissolution of the cement sample was also examined. The range of temperature used was 28°C-80°C. The fraction of the cement sample

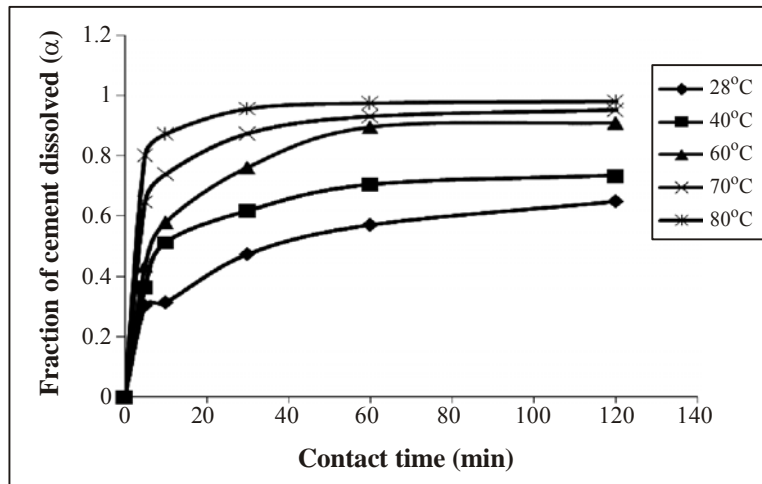dissolved at various temperatures and at corresponding contact time of leaching is represented in Fig. 3.

Fig. 3: Plot of fraction of cement dissolved vs contact time at different temperature

Experimental conditions: HCl concentration = 0.5M, Temperature = 28°C-80°C, Stirring speed = 200 rpm, Particle size = ≤ 0.1 mm.

As seen from Fig. 3, an increase in temperature brings about a steady increase in the hydration dissolution reaction rate that leads to increase in the amount of cement sample dissolved.

The rate of the dissolution of the cement sample was analyzed by using two shrinking core models. These are:

$$1-(1-\alpha)^{1/3} = k_1 t \qquad \qquad \qquad …(10)$$

based on the assumption that the rate controlling step occurs by surface chemical reaction.

$$1-\tfrac{2}{3}\alpha - (1-\alpha)^{2/3} = k_2 t \qquad \qquad \qquad …(11)$$

based on the assumption that the rate controlling step is diffusion through a semi-permeable product layer[12].

Where α is the fraction of the cement sample dissolved, t is the contact time (min), k_1 and k_2, are the rate constants. Both the data in Figs. 2 and 3 were fitted to equations (10 and 11), respectively. It was found that only the plotting of $1-\tfrac{2}{3}\alpha-(1-\alpha)^{2/3}$ against time at

different HCl concentrations and temperatures, respectively gave straight lines with perfect correlation (of ≈ 0.9981). (See Figs. 4 and 5).
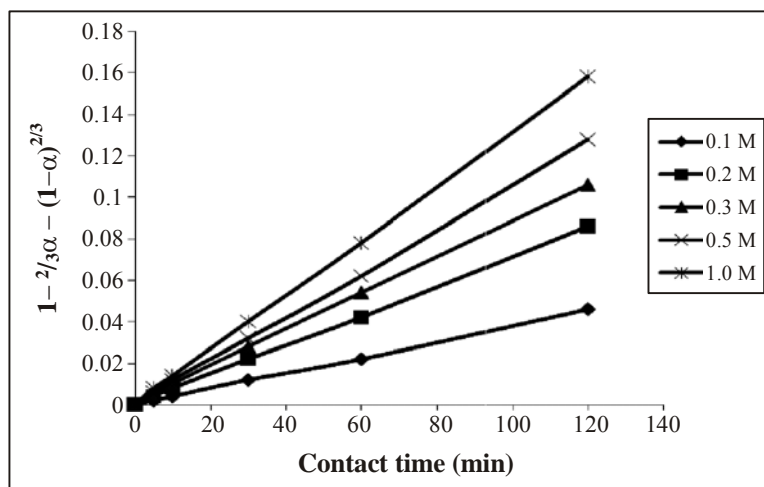

Fig. 4: Plot of 1-2/3 α-(1-α)$^{2/3}$ vs contact time at different HCl concentration
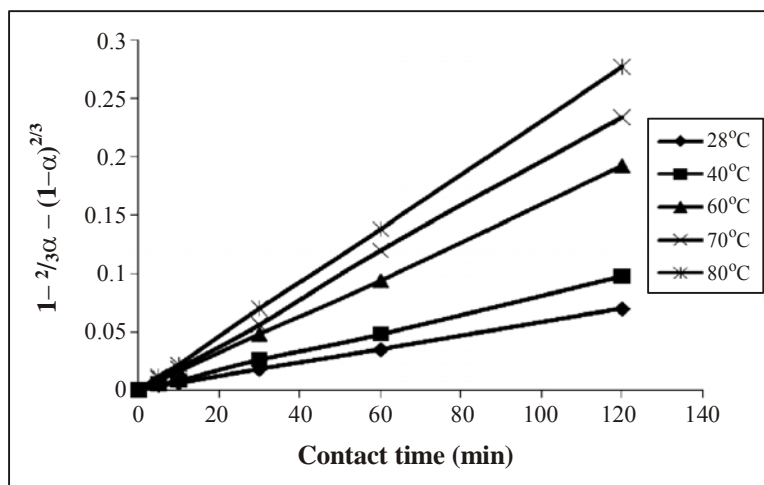
Experimental conditions: Same as in Fig. 2.

Fig. 5: Plot of 1-2/3 α-(1-α)$^{2/3}$ vs contact time at different temperature

Experimental conditions: Same as in Fig. 3.

The mechanism of the hydration dissolution; therefore, follows the diffusion model.

That is, H^+ ion concentration diffuses from the bulk of the solution into the cement sample. This result was in accordance with a work on hydration of a material[14], where the authors proposed that the deceleration period for the hydration of cement follows a diffusion controlled process using Jander equation:

$$[1-(1-\alpha)^{1/3}]^2 = kt \qquad \qquad …(13)$$

The slopes of the plot in Fig. 4 were then evaluated and these correspond to the rate constant (k_s), from which ln k were plotted against ln [HCl] as represented in Fig. 6.
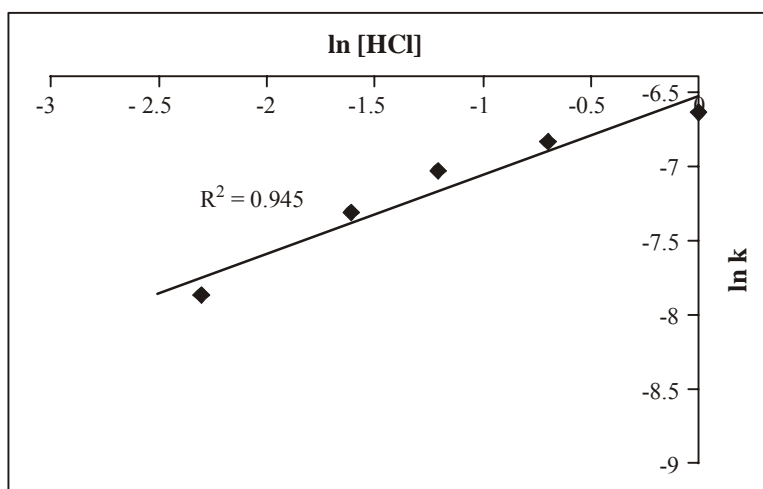

Fig. 6: Plot of ln k vs ln [HCl]

The slope of the plot in Fig. 6 represents the order of the reaction in which a value of 0.77, which is close to unity was obtained. Therefore, the reaction order with respect to HCl concentration is assumed to be first order relation.

Furthermore, the slopes of the line in Fig. 5 were also evaluated as apparent reaction rate constant, k. The Arrhenius plot, ln k plotted against the inverse of the temperature ($^1/_T$) is shown in Fig. 7. The activation energy and the Arrhenius constant were then determined (Fig. 7).

The activation energy evaluated from the slope of the plot in Fig. 7 was 26.3 kJ/mol and this value suggests a diffusion controlled mechanism. Finally, the re-plot of Fig. 7 from the origin[13] gave Arrhenius constant of 4.13 s^{-1} for the hydration dissolution process.
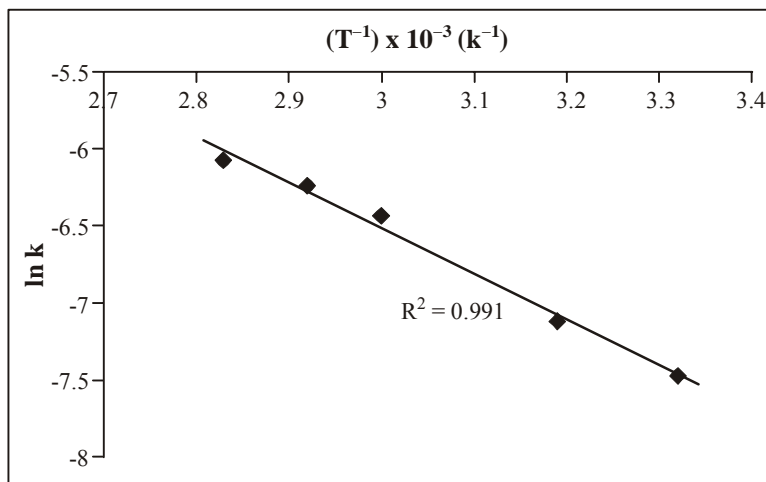
Fig. 7: Plot of ln k vs $(T^{-1}) \times 10^{-3}$ (k^{-1})

CONCLUSION

From the results obtained in this study, it is seen that the rate of cement hydration dissolution in acid media is dependent on H^+ ion concentration, whose reaction order approximately equal to one. Also the result of ICP-MS for the cement sample showed that the elemental composition is amenable with the available standard/specification as evidenced by the phase characterization using X-ray diffractometry. Finally, the dissolution hydration study gave rise to about 26.3 kJ/mol activation energy, which affirmed the diffusion reaction mechanism and a value of 4.13 s^{-1} was also obtained as the Arrhenius constant for the process.

ACKNOWLEDGEMENT

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