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Determination of the Rate of Calcination During Cement Production

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Abstract: Rate data were collected for calcinations during cement production for 4 years at the same time intervals. The amount of $CaCO_3$ consumed in tons was plotted against time in minutes. The plots gave good numerical fit (R^2>0.99) for all the model equations studied but the parameter estimates for K, C_{AO} and n varied widely (>5%) for all rate equations except the rate equation for zero order reaction which has an average rate constant of 1.41275 tons min^{-1} and an average percentage deviation of 3%. Calcination is a zero order reaction based on the equation, C_{AO}-C_A = Kt with an average reaction rate constant of 1.41275 tons min^{-1}. This rate model will serve as a basis for the design of rotary kiln for calcinations processes. The model equation obtained from this research may also be used to simulate and optimize processes for cement production.

Key words: Calcination, cement, rate, decomposition, limestone, clinker, calcium carbonate

INTRODUCTION

Calcination is the process of heating a substance to a high temperature but below its melting point to bring about thermal decomposition or a phase transition in its physical or chemical constitution (Bunch, 2004). It is one of the 109, all chemical processes which aid in the transformation of substances and a vital process in the production of cement (Gupta and Salhigamorthy, 1999; Bunch, 2004; Levenspiel, 2006). The burning of limestone during cement production brings about the evolution of carbon dioxide which contributes 5% of the world's anthropogenic carbon dioxide emission, with about 900 kg CO_2 emitted for every 1000 kg of cement produced (Liptrot, 1984; Gupta and Salhigamorthy, 1999; Mahasenan *et al*., 2003). Here, the thermal decomposition of limestone occurs, giving off the carbon dioxide and forming quicklime (calcium oxide) which is mixed with other raw materials in the slurry to form clinker (McCabe and Smith, 2005; Levenspiel, 2006):

$$CaCO_3(s) \xrightarrow[800-900^0C]{\text{Heating}} CaO\ (s) + CO_2\ (g) \qquad (1)$$

The rate of thermal decomposition of limestone is the rate at which the calcium trioxocarbonate (IV) decomposes thermally or the rate at which calcium oxide is formed or carbon (IV) oxide is evolved. For every mole of carbon dioxide evolved, one mole of calcium oxide is also produced and one mole of calcium trioxocarbonate (IV) is consumed (Richardson, 2006). The dimensions of the rate constant in the form of K for the nth order are $(time)^{-1}$ $(concentration)^{1-n}$. The main raw material in cement manufacture is the clinker, an artificial rock made by heating limestone and other raw materials in specific quantities to a very high temperature in a kiln (Felder-Casagrande *et al*., 1997). There are four components that make up the clinker in the kiln:

- Tricalcium Silicate = 3 $CaOSiO_2$, (Alite,C_3S)
- Dicalcium Silicate = 2 $CaOSiO_2$, (Belite,C_2S)
- Tricalcium Aluminates = 3 $CaOAl_2O_3$, (C_3A)
- Tetra calcium Alumina Ferrite = 4 $CaOAl_2O_3Fe_2O_3$ (C_4AF)

The various types of Portland cement generally require different proportions of these four components (Gilchrist, 1989; Hewlett, 1998). Evaporation and pre-heating is used to remove moisture and raise the temperature of the raw mix preparatory to calcining which takes place at a temperature of 800°C and breaks the calcium carbonate down into calcium oxide and carbon dioxide which evolves in the process.

Clinkering completes the calcinations stage and fuses the calcinations raw mix into hand nodules resulting into small grey pebbles. Kiln temperature in the burning zone ranges from 1350-1430°C and retention times in this zone are 4-6 sec. Clinkering is critical to the quality of cement and requires accurate control of energy input (Gupta and Salhigamorthy, 1999; Hewlett, 1998; Mahasenan *et al*., 2003). Calcination is done:

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- To drive off water, present as absorbed moisture or as water of crystallization
- To drive off carbon dioxide (as in limestone into lime in a rotary cylindrical kiln), sulphur dioxide or other volatile constituents
- To oxidize (oxidation calcinations) a part or the whole of the substance commonly used to convert metal sulphide ores to oxides in the first step of recovering such metal as zinc, lead and copper
- To reduce (reductive calcinations) metal from their ores (smelting) (Anusiem, 2000)

The purpose of this study is to determine the rate of calcinations in cement production so as to help in the simulation, optimization and control of the process of cement production.

MATERIALS AND METHODS

The data were sourced from West African Portland Cement Plc, Sagamu, Ogun state, Nigeria. The amounts of $CaCO_3$ consumed at specified time intervals (which are equivalent to the amount of CaO produced) from 2002-2005 are shown in Table 1.

Let C_A represent the amount of $CaCO_3$ available at any time, t and C_{AO} the initial amount of $CaCO_3$ available. The amount of $CaCO_3$ consumed can be represented as (C_{AO}-C_A):

$$\frac{dC_A}{dt} = -KC_A^n \quad (2)$$

$$\frac{dC_A}{C_A^n} = -Kdt \quad (3)$$

$$\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A^n} = -Kt \quad (4)$$

Table 1: Amount of $CaCO_3$ consumed during calcinations in tons

Time (min)	2002 (tons)	2003 (tons)	2004 (tons)	2005 (tons)
0	0.00	0.00	0.00	0.00
1	1.37	1.39	1.30	1.35
2	2.95	2.79	2.90	2.60
3	4.56	4.11	4.40	3.77
4	5.98	5.44	5.85	4.91
5	7.45	6.99	6.54	6.41
6	8.85	8.39	8.22	8.11
7	10.48	9.96	9.64	9.38
8	11.93	11.49	11.23	10.34
9	13.45	12.44	12.79	11.84
10	15.03	13.89	14.04	13.39
11	16.54	15.29	15.61	15.04
12	18.14	16.79	17.09	16.79

There are three special cases: for n = 0 we have:

$$C_{AO}-C_A = Kt \quad (5)$$

For n = 1, we have:

$$C_{AO}-C_A = C_{AO}\,(1-\exp(-Kt)) \quad (6)$$

For 0<n<1 or n>1, we have:

$$C_{Ao}^{1-n} - C_A^{1-n} = (1-n)Kt \quad (7)$$

Since, $C_{AO}>C_A$, most of the time, it can be shown from binomial expansion that due to cancellations from alternating addition and subtraction of terms and the negligible effect of (C_{AO}/C_A) terms for higher powers, Eq. 7 can be approximated by Eq. 8:

$$(C_{AO} - C_A)^{1-n} = (1-n)Kt \quad (8)$$

$$(C_{AO} - C_A) = ((1-n)Kt)^{(1/(1-n))} \quad (9)$$

Analysis of data: The data was analyzed using the curve fitting toolbox of MATLAB 7.0 to obtain graphical and numerical fit results for plots of (C_{AO}-C_A) against time (t), using Eq. 5, 6 and 9 without further modification. Numerical fit results for all equations are studied are shown with the graphical fit results for Eq. 5. Table 2-4 and Fig. 1-4. The best model was chosen based on the following criteria:

Table 2: Numerical fit results for zero order rate model from 2002-2005

Years	Equations	R^2	K (tons min^{-1})	Mean deviation for K (%)
2002	C_{AO}-C_A = Kt	0.9998	1.500	6.176
2003	C_{AO}-C_A = Kt	0.9995	1.398	1.044
2004	C_{AO}-C_A = Kt	0.9986	1.408	0.336
2005	C_{AO}-C_A = Kt	0.9967	1.345	4.796

Table 3: Numerical fit results for rate model with order one (n = 1) from 2002-2005

Years	K (mins^{-1})	C_{AO} (tons)	R^2	Mean deviation for K (%)	Mean deviation for C_{AO} (%)
2002	0.0007959	1891.0	0.9998	14.17	9.80
2003	0.0018910	745.8	0.9995	103.93	64.43
2004	0.0006432	2195.0	0.9985	30.64	4.70
2005	0.0003789	3554.0	0.9966	59.14	69.52

Table 4: Numerical fit results for rate model with order n (0<n<1 or n>1) from 2002-2005

Years	K	Reaction order (n)	R^2	Mean deviation for K (%)	Mean deviation for n (%)
2002	1.467	0.01403	0.9999	7.670	44.775
2003	1.398	3.542e-9	0.9995	2.606	100.000
2004	1.366	0.02015	0.9988	0.257	20.685
2005	1.219	0.06744	0.9985	10.532	165.460

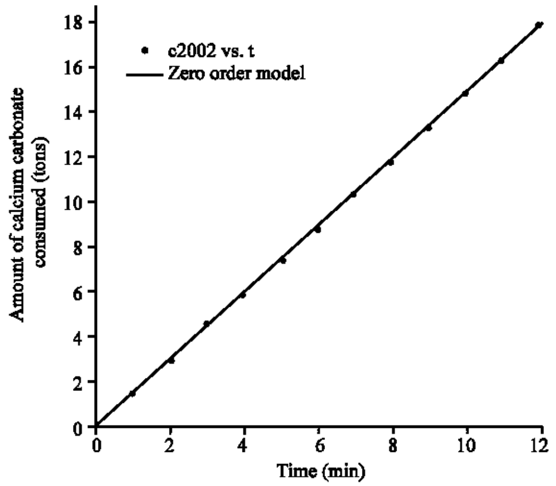

Fig. 1: C_{AO}-C_A vs. t for year 2002

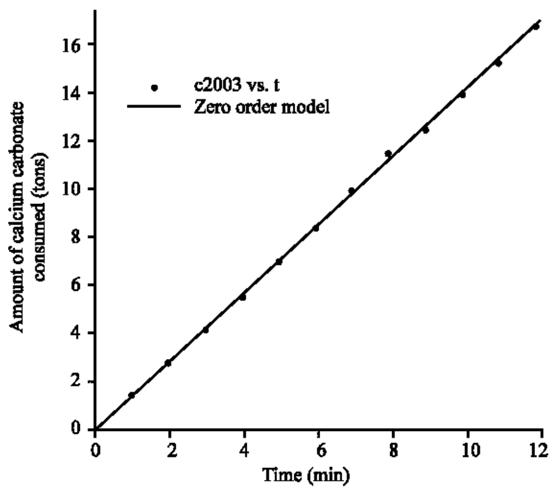

Fig. 2: C_{AO}-C_A vs. t for year 2003

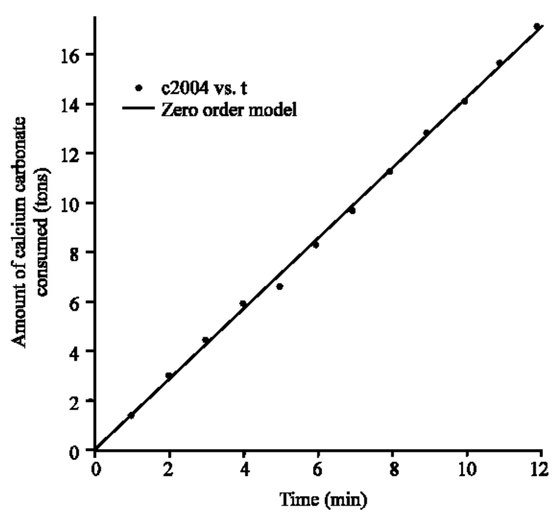

Fig. 3: C_{AO}-C_A vs. t for year 2004

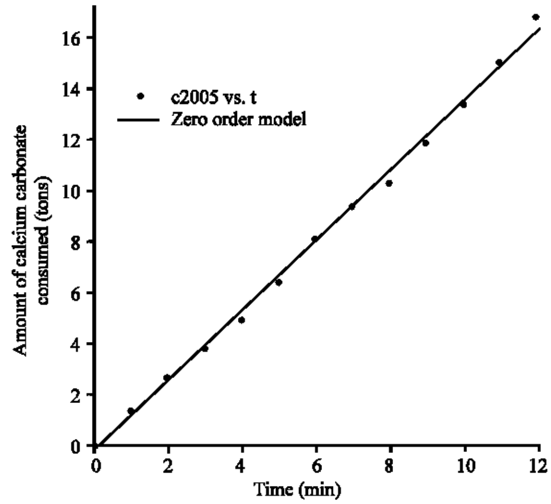

Fig. 4: C_{AO}-C_A vs. t for year 2005

- Numerical fit results for K, n and C_{AO} in Eq. 5, 6 and 9 for each year should not vary widely, an average percentage deviation $\leq$5% from the mean value is acceptable
- The coefficient of determination (R^2) should be $\geq$0.99

RESULTS AND DISCUSSION

All the rate models gave good fits (R^2>0.99) to the experimental data. The rate equation for nth order reaction gave a good fit ($0.9985 \leq R^2 \leq 0.9999$) with the average order of reaction as 0.0254 and an average reaction rate constant of 1.3625. The average percentage deviations for the order of reaction and rate constant are 82.73 and 5.266%, respectively. The model equation for nth order reaction model is not acceptable due to the wide variation in the kinetic parameter estimates, especially the order of reaction.

The rate equation for the zero order reaction rate model gave a good fit ($0.9967 \leq R^2 \leq 0.9998$) with an average reaction rate constant of 1.41275 tons min^{-1}. The average percentage deviation for this rate constant is 3.088%. The rate model for the first order reaction model gave a good fit ($0.9966 \leq R^2 \leq 0.9998$) but the values of the rate constant, K and C_{AO} varied widely, with average percentage deviations of 51.97 and 37.1125%, respectively which also makes the model equation unacceptable.

CONCLUSION

Calcination is a zero order reaction, based on the equation, C_{AO}-C_A = Kt, with an average rate constant of

1.41275 tons min^{-1}. This rate model will serve as a basis for the design of rotary kiln for calcination processes. The model equation obtained from this research may also be used to simulate and optimize processes for cement production.

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