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Calcium hypochlorite from Nigerian limestone

I.A. Musa*, E. G. Shide[3], and C. E. Gimba[2]
[1]*Department of Chemistry Adamawa State University, Mubi*
[2]*Department of Chemistry, Ahmadu Bello University, Zaria*
[3]*Department of Chemical Engineering Ahmadu Bello University, Zaria*

ABSTRACT

Calcium hypochlorite was laboratorial prepared by bubbling chlorine gas into suspended aqueous slurry solution of locally sourced Ca $(OH)_2$, at constant mass flow rate of 0.4 g/s for time intervals 5 s (5) 20 s at 0.5 atm. The concentration of the preparations varied between 4.16–15.4 g/dm^3 corresponding to available chlorine (ACHL) of 51 – 63%. This range falls favorably with commercial products of solid chlorine from Clear Tech Industries Inc., 2303 Hansel man Avenue, Saskatoon SK S71 5Z3, Canada (product produced March 3, 2003; CAS Number 7778-54-3; ACHL, 60-80%). Our results have the potentials of sparking indigenous technology for development of industrial chemicals from our abundant local natural solid minerals resources, when the processes involved are optimized.

Keywords: Limestone, hypochlorite, available chlorine, indigenous technology.

*Author for correspondence

INTRODUCTION

Calcium hypochlorite, $Ca(OCl)_2$, is generally produced by the chlorination of aqueous solution of hydrated quicklime that is obtained by calcination of limestone [1-7]. The product is of wide range of applications in chemical industrial processes amongst are: pulp and textile industries, water treatment sectors, hospital equipment sanitation, artificial beauty industries [3,5-9,10,11]. There have been great deal of studies on the production of hypochlorites as pointed [10]. Most of these contributions have concentrated on alkali hydroxide for both hydroxyl and base metals sources for the hypochlorites preparations. The Alkali-Source- Methods (ASM) are limited by:

(i) lack of constant availability necessitating cost ineffectiveness,
(ii) products are always characterized by fast degradation due to instability to most common storage conditions and
(iii) commercial and more stable forms of the products contain only 5-15% the essential ingredient, implying importation of 95-85% water apart from the container.

The solid hypochlorite from calcium hydroxide is more stable, cost friendlier, easily handled and most suitable for tropics under harsher temperature environments [7].

Despite literature abundance, the mechanisms and actual rates for the interaction of Chlorine (Cl_2) and aqueous solutions of both alkali and alkaline metals remain insurmountable; especially when industrial scale production operations are the ultimate targets. Although appreciable breakthroughs have been recorded in commercializing hypochlorites production (www.ppgchloralkali.com**,** www.kvaerner.com/chemestics/chemplant/calchypo/calchypo.htm and Olin Mathieson in [7], the necessary technology is only available to the developers and only products of these technologies are sold in common markets; while the technologies are protected and continuously being modified. The current attitudes of developing countries (Nigeria inclusive) ,which thirst for most recent research breakthroughs in place of developing our own technologies only keep us perpetual dependents on foreign goods and services at the expense of our true independent and self reliance that has resulted in widespread poverty in the midst of plenty (http://www.aeseda.psu.edu).

In this work, efforts are made towards the indigenous technology for production of calcium hypochlorite, an industrial chemical for a wide range of applications, which has continue to enjoy importation into our country, Nigeria; even though there exist sufficient potentials for its manufacture.

THEORY SECTION

Sources of calcium hydroxide

The parent ore for the commercial manufacture of calcium hydroxide, $Ca(OH)_2$, is calcium carbonate, $CaCO_3$. When heat is applied to the limestone; calcium oxide, CaO, and carbon dioxide, CO_2, are released, Equation 1a. However, noncommercial sources are available in which the $CaCO_3$ content is low, Equation

1 b & c. The stoichiometric equations below demonstrate some production steps involved in purification and production of $Ca(OH)_2$:

(i) $CaCO_3 \rightarrow CaO + CO_2$
(ii) $Ca(HCO_3)_2 + heat \rightarrow CaO + 2CO_2 + H_2O$
(iii) $Ca.Mg(CO_3)_2 + heat \rightarrow CaO.MgO + 2CO_2$
(v) $CaO + H_2O \rightarrow Ca(OH)_2$ ……..1

Sources of chlorine

Chlorine was first discovered and known as dephlogisticated marine acid by Carl Wilhelm Scheele in 1774 [12]), when he reacted manganese (iv) oxide, MnO_2, with hydrochloric acid, HCl:
$MnO_2 + Hcl \rightarrow MnCl_2 + 2H_2O + Cl_2$ ……. 2

After 36 years later, Sir Humphry Dave in 1810, established chlorine as an element and its present name; chlorine [12]. Chlorine can be produced in smaller quantities for laboratory experiments, amongst include:

(i) $2KMnO_4 + 16HCl \rightarrow KCl + MnCl_2 + 8H_2O + 5Cl_2$
(ii) $HNO_3 + 3HCl \rightarrow NOCl_2 + 2H_2O$
(iii) $COCl_2 \rightarrow CO + Cl_2$ …………… 3

Laboratory preparation by decomposition of phosgene should not be adopted without proper safety equipment and wares, because $COCl_2$, carbon monoxide, CO, and Cl_2 are poisonous; in addition to difficulty in detecting $COCl_2$ that is colorless and odorless. However, the profitable source of Cl_2 production is an electrolytic process using NaCl, in which NaOH is produced as the main product and Cl_2 evolved as a by-product.
(i) $2Cl^- - 2e \rightarrow Cl_2$, at anode
(ii) $2H^+ + 2e \rightarrow H_2$, at cathode
(iii) $Na^+ + OH^- \rightarrow NaOH$ (from solution)
(iv) $2Na\text{-}Hg + 2H_2O \rightarrow 2NaOH + H_2 + 2Hg$
(from Na-Hg)…..4

Under reduced pressure, NaOH solution is evaporated to 50% strength, impurities reduced, and this is further strengthened to 70% and finally dewater by heating to 500°C. When Cl_2 is bubbled into solution of $Ca(OH)_2$, the following results:
$2Cl_2 + 2Ca(OH)_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$ ……5

EXPERIMENTAL

Material

Chlorine, BDH grade, was purchased from commercial source in Kaduna town, Kaduna state, Nigeria. Hydrated $Ca(OH)_2$ was obtained from the National Research Institute for Chemical Technology (NARICT), Zaria; being product produced by the Institute from Jakura limestone deposit in Kogi state of Nigeria and all the other reagents used were of analytical grade and obtained from BDH. All the glass wares were scrupulously washed and dried under laboratory conditions before use.

METHODS

Degritting of calcium hydroxide

Raw samples, 100 g each, weighed (using BFF-40-010V Top weighing Metttler Balance and SMJ-851-V spatula stainless steel pk/5) into various volumes of distilled water and stirred using a motor stirrer (KQPS/20, Citeco Ltd., England)., in triplicate, the suspensions were screened through a 0.074 mm mesh to determine point suitable for grits removal, which was used to obtain screened sample. The results from this experiment are reported under Figure 1.

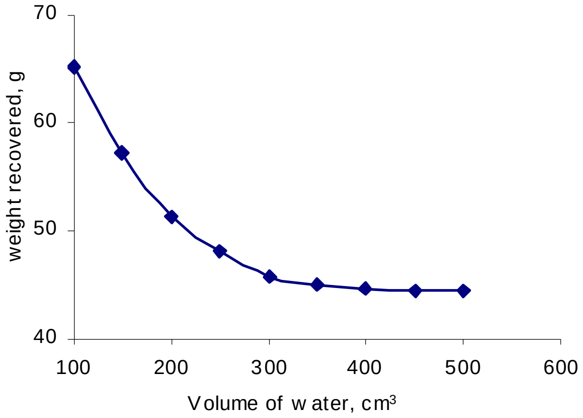

Figure 1: Calcium hydroxide screening profile

Solubility test for unscreened and screened $Ca(OH)_2$

Saturated solutions of both unscreened and screened samples were carefully made in varying sucrose solutions and titrated against 0.364 M HCl using methyl orange as indicator. Average values for three experimental runs were made. The experiments were repeated for different sucrose solutions and the results recorded under results and discussion section.

Calcium hypochlorite mixture analyses

Two saturated solutions, 300 cm^3 each: A, containing screened $Ca(OH)_2$ and B, containing screened $Ca(OH)_2$, in 35% sucrose solution of equal concentration of 20w/w% $Ca(OH)_2$; particles sized to 7.5 Fm using laboratory test sieve (BS 410, Pat. No. 667924, Ser. No. 249962; Endecotts Ltd., London, England). Chlorine (commercial source), considered pure, was passed unto the suspension that was stirred, 350 rpm, using motor stirrer (KQPS/20, Citeco Ltd., England). The time the reaction was varied, 5(5)20s at a constant flow rate of 0.4 g/s (5) and examination conducted for ACHL, $Ca(OH)_2$ and calcium chloride, $CaCl_2$. The concentration of hypochlorite was determined using standard method ; concentration of Ca $(OH)_2$ was determined using pH meter and the calcium chloride concentration determined using Mohr's method [13]. The results are presented in Figure 2.

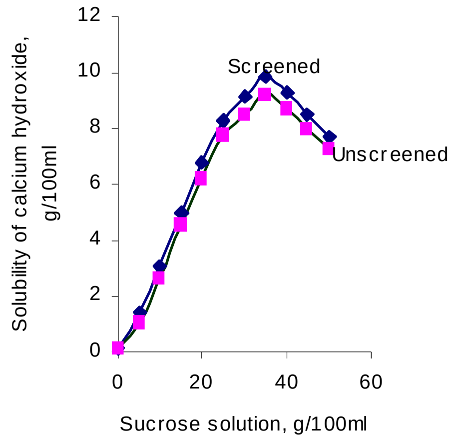

Figure 2: Comparative solubility of calcium hydroxide in sucrose solutions

RESULTS AND DISCUSSION

Calcium hydroxide generally has low solubility in water ranging form 0.07% at 100°C to 0.19% at 0°C. These values are worsened by presence of under/over burned of rocks or impurities that had escaped calcination. At NARICT, the condition for high purity $Ca(OH)_2$ cannot be achieved due to: nature of the limestone, combustion control, hydration techniques and the defects of kiln design. However, for research purposes, the product was beneficiated before use. The results from beneficiation confirmed the presence of grits evident in gradual decrease in weight beneficiated as function of water volume reported in Figure 1 To determine an optimum point for beneficiation, the constant weight beneficiated was used and this point is 1:4 in respect of sample to water. The results of solubility test in different sucrose concentration are presented in Figure 4.2.0. The results showed increase in solubility of calcium hydroxide when sucrose solutions are used instead of pure water. At ambient temperature of 25°C and atmospheric pressure, the solubility is increased from reported value of 0.16g/100g to 9.2g/100g for unscreened sample and 9.9g/100g for screened sample at 35% sucrose concentration; representing respectively, an increment of 9.04-9.74g/100g. These results corroborate the report that sucrose exerts the greatest influence on the solubility of lime; that at 35% sucrose concentration, the increase is 10.1g/100g. The results on solubility test also indicate that improved solubility is achieved by beneficiation of up to 8% at 35% sucrose concentration.

The results of Figures 1 and 2 show that chlorination of calcium hydroxide solutions with 35% sucrose concentration should provide better hypochlorite due to higher solubility of calcium hydroxide; this was not observed since the chlorination could not give the characteristic dark yellow colour on addition of potassium iodide to indicate the release of iodine from iodide salt. These solutions were subjected to pH examination for the 5(5)20s time intervals and respective pH's of 5.5, 2.5, 2.3 and 2; all acidic! At pH below 6.0, over 95% of available chlorine are resent as hypochlorous acid (HOCl) that has very low dissociation constant of 3.2×10^{-8}, liberation of OCl^-, impeded. However, chlorination of solution of pure aqueous calcium hydroxide solution yielded results presented in Table 1. The theoretical chlorine was calculated using the dimension of the pipe (0.01m, ID), pressure (0.5 atm) and the time (5, 10, 15 20s); this showed progressive increase throughout the period of investigation from 2.03-8.12g Cl_2. Such results are misleading in designs since they indicate no equilibrium; necessitating large equipment in the midst of limited materials that can be avoided [14]. The actual (practical) chlorine present in our preparation after 15s retention time is 3.82 g Cl_2, representing the maximum in our preparation and also 63% Cl_2 introduced. The rest represent either loss due to side products (calcium chloride amongst, which varied between 2-3%) or unabsorbed, the later situation is an unfriendly environmental warning. Our results cannot provide optimum values for industrial applications due to the short interval of contact [1], also other side products

Table 1: Analysis of Chlorinated Calcium Hydroxide

Time, s	Mass of theoretical chlorine, g	Mass of practical chlorine, g	% Available chlorine,
5.0	2.03	1.03	50.90
10.0	4.06	2.23	55.02
15.0	6.09	3.82	62.76
20	8.12	1.55	19.09

were not investigated. Optimization of parameters for hypochlorite production should be pursued.

In conclusion, our results have potentials in development of indigenous technology for calcium hypochlorite production.

REFERENCES

1. C. Terence, Y. Rong, T.L. David and H.T. Joo (2005). Hydrated Lime Reactions with HCl under Simulated Flue Gas Conditions. *Ind. Eng. Chem. Res.*, **44**: 3742- 3748.
2. D.D. Tuan, H. Manh, and L.N. Kien (2005). Sorption of Na^+, Ca^{2+} ions from aqueous solution onto unbleached kraft fibers – Kinetics and equilibrium studies. *Journal of Colloid and Interface Science*. **287**: 438-443; www.elsevier.com/locate/jcsi
3. G. F. Qin, Z.Y. Li, X.D. Chen and A.B. Ressell (2002). An experimental study on NaClO generator for anti-microbial applications in the food industry. *Journal of Food Engineering*, **54**: 111-118; www.elsevier.com/locate/jfoodeng
4. R. Sharmistha, T.R. Garry and G.B. Theodore (2001). Chlorine Absorption in S (IV) Solutions: USEPA-600/R-01-054.
5. S. Bashtan, V.V. Goncharuk, R.D. Chebotareva, and V. N. Belyakov (1999). Production of sodium hypochlorite in an electrolyser equipped with a ceramic membrane. *Desalination* **126**: 77-82; www.elsevier.com/locate/desal
6. A. Kraft, M. Blaschke, D. Kreysig, B. Standt, F. Schroder and J. Rennnau (1999). Electrochemical water disinfection. Part II: Hypochlorite Production from potable water, chlorine consumption and the problem of calcareous deposit. *Journal of Applied electrochemistry*, **29**: 895-902, Kluwer Academic Publishers. Netherlands.
7. Kirk-Othmer, (1973): Encyclopedia of Science and Technology, John Willey and Son, Vol. 3. 3rd edition, 34, 123; 347 – 403. New York.
8. A. Khelifa, S. Moulay, F. Hannane, M. Benslimene and M. Hecini (2004). Application of an experimental method to study the performance of electro chlorination cell. *Desalination*, **160**: 91-98; www.elsevier.com/locate/desal
9. K. Merritt, V.M. Hitchins and S.A Brown (1999). Safety and Cleaning of Medical Materials and Devices. FDA Centre for Devices and Radiological Health, Division of Life Science, HFZ 112, Rockville, Maryland 20852.
10. S. A. Sami, B. R. Edward and C. S. Orville (1996). Absorption of Chlorine into Aqueous Bicarbonate Solution and Aqueous Hydroxide Solution, *AlChE. J.*, **42**: 671 – 682.
11. S. Elzo, K. Hidehiro, L. Choulho and F. Nobuya (1985). Gas- Liquid Mass Transfer Characteristics in Bubble Column with Suspended Sparingly Soluble Fine Particles. *Ind. Eng. Chem. Process Des. Dev*. **24**: 255-261.
12. J.N. Wilson and A.B. Newall (1970). General and Inorganic Chemistry, 2nd ed., Cambridge University Press, New York.
13. S.B Dikko, B.A. Fodeke, and Z. Tryvianski (1983). IJMB Laboratory Chemistry Manual. Oracle publishers. Zaria-Nigeria.
14. T.I. Mku (1994). A non-parametric method for particle settling velocity determination in a slurry bubble column. *The Chemical Engineering Journal*, **54**: 1-6.