

Production of Gypsum from Clamshells and Waste Acid Recovered from End-of-Life Lead Acid Batteries*

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Gohoho, H. D. and Dankwah, J. R. (2019), "Production of Gypsum from Clamshells and Waste Acid Recovered from End-of-Life Lead Acid Batteries", *Ghana Mining Journal*, Vol. 19, No. 1, pp. 66 - 71.

Abstract

Gypsum exists in the Dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) and the Anhydrite (CaSO_4) forms. The exploitation of the natural rock form deposit of gypsum is on the increase, necessitating the need to find alternative and efficient sources of gypsum so as to sustain all the industries dependent on gypsum as raw material. This work investigates the production of gypsum from clamshells and waste sulphuric acid from end-of-life car batteries. Clamshells obtained from the Volta Region of Ghana were calcined at a temperature of about 1000°C with a view of producing CaO which was pulverised to particle size of 96 % passing $106\ \mu\text{m}$. Samples of the Pulverised Clam Shells (PCS) were then reacted with five different concentrations of the Waste Battery Acid (WBA). The reaction was observed to be very exothermic; a temperature of 101°C was obtained for the 6.5 M concentration of WBA. The resulting mixture was filtered and an XRD analysis was performed on the oven dried residue to ascertain its composition. The findings from the work revealed that 100 g of pulverised clam shells produced an average of 58.08 g of calcined product and 134 g of gypsum. Peaks of SiO_2 and CaCO_3 in the XRD diffractogram of the gypsum indicated that the reaction between PCS and WBA was incomplete. Conclusively, the results from the XRD analysis showed peaks of the three forms of gypsum that was successfully produced.

Keywords: Net Present Value, Internal Rate of Return, Sensitivity Analysis, Risk Analysis

1 Introduction

Clam is the general common name of any molluscs within the class Bivalvia. Clams are bivalves having two shells of equal size connected by two adductor muscles and having burrowing foot. The sale of clams is a lucrative business for the indigenes living along the Volta River or lake in Ghana. It is known as "Adordi" by the local people. Clam shells are not consumed in Ghana so once the food is taken out; the shells are stockpiled for sale. The shells can be stockpiled for months awaiting buyers due to lack of readily available processing technology.

The locals in the community use the shells in poultry feeds as a source of calcium and also as feedstock in white wash paint, soil conditioning, erosion checks and concrete works. Huge tonnes of shells lie ideal in the community when not purchased. The shell heaps have visual impacts, have foul stench and serve as breeding grounds for mosquitoes and some wild reptiles like snakes, etc.

Clam shells and other sea-related shells contain predominantly calcium carbonate (CaCO_3) and some silica (SiO_2) used in the production of lime (CaO) (Nordin *et al.*, 2015), which can be further transformed into gypsum (calcium sulphate Dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). (Ni'mah *et al.*, 2018). Gypsum is the first mineral to crystallize when sea water evaporates. (Warren, 2006). It is a very soft

mineral and is second on the Mohr's scale of hardness. (Thorman, 1973) Gypsum can be produced by drying, grinding and calcination of the natural rock to produce natural gypsum or by the synthetic way which can be done in several ways to produce synthetic gypsum. Flue Gas Desulphurization (FGD) with lime or limestone is one of the means of producing synthetic gypsum. Gypsum plays an important role in the cement industry as the main retarding and setting agent, plasterboards industry for decors and the agriculture industry as a soil conditioner and a source of minerals for some plants like peanuts. Waste acids can be recovered from end-of-life car batteries in the form of highly concentrated sulphuric acid. After the useful life of the batteries, the acid and other components are improperly disposed into the environment. Countries with strict environmental regulations are against the improper disposal of these waste car batteries into their land fill sites. In Ghana, the acids are just discarded into the environment; these acids are highly concentrated and contain traces of lead metal. Lead is a heavy metal which, if not properly disposed, can leach into underground water and the ecological cycle (food chain). Artisanal and Small Scale Gold Miners use the acid to further clean their gold after smelting. Large volumes of these acids are generated by the automobiles and Uninterrupted Power Supplies; hence there is the need to find an environmentally sustainable way of disposing and recycling the acid.

*Manuscript received September 6, 2018

Revised version accepted June 24, 2019

<https://dx.doi.org/10.4314/gm.v19i1.8>

Buasri *et al.* (2013) observed that the calcination of various forms of sea shells (mussel, cockle and scallop) at temperatures around 1000 °C leads to the formation of calcium oxide (up to about 99.170 wt% CaO). Ni'mah *et al.*, (2018) investigated the production of gypsum from blends of calcined samples of clamshell and eggshell. They concluded that optimum amounts of gypsum could be produced from a blend consisting of 20 wt% eggshell, 20 wt% clamshell, 20 wt% H₂SO₄ and 40 wt% H₂O. Ni'mah *et al.*, (2016) had earlier investigated the production of gypsum board from calcined eggshell waste, concluding that 35% calcined material, 50% aquadest and 15% sulfuric acid, with an elapsed time of 5.5 mins producing the best results. In all the investigations mentioned above, the H₂SO₄ used was not a waste material; it was purchased fresh by the authors. The specific objectives of this research are therefore to reduce the environmental impacts of clamshells heaps and waste battery acid in the community and also to produce gypsum from pulverised clamshells (PCS) using waste concentrated sulphuric acid (H₂SO₄) from car battery.

2 Resources and Methods Used

2.1 Preparation of Clam Shells

Samples of the clamshells (Fig. 1) were collected from Sogakope in the Volta Region of Ghana. These were washed thoroughly with clean water to remove the dirt and mud attached to some of the shells. The thoroughly washed shells were then sun dried for seven (7) days to remove any physically bound water.



Fig. 1 Samples of Clamshells before Calcination

2.2 Calcination of the Clam Shells

A representative sample was taken for calcination at temperatures of 1000 °C. The material was calcined at 1000 °C for 2 hours to drive off all volatiles as well as expel CO₂ associated with the clam shell samples. Samples of the calcined clamshells are shown in Fig. 2.



Fig. 2 Samples of Calcined Clam Shells

2.2.1 Weight loss associated with Calcination Process

As the calcination process drives off chemically bound water, volatiles, organic components and also some gases, the weight loss that occurred during the calcination process was determined.

2.2.2 Pulverisation of the Calcined Clam Shells

The calcined clam shells were allowed to cool down and were subsequently pulverised in a ball mill for 30 minutes using a steel ball loading of mass 14 kg. Samples of the pulverised clamshells are shown in Fig. 3.



Fig. 3 Pulverized Clam Shells

2.3 Solubility Analysis and pH of the CaO Produced

About 100 g of the pulverised clamshells were dissolved in 1000 ml of water to determine the solubility of the calcium oxide (CaO) produced. The resulting solution was poured into a 5 litre bottle and set for bottle roll for 24 hours.

After 24 hours, the solution was filtered and the residue was dried in an oven to remove all moisture; the change in the mass of the 100 g sample used for the test establishes the solubility of the pulverised clam shells to be around 5 g/L. The pH of the filtrate together with the solids was measured; a pH of 12.1 was recorded.

2.4 Particle Size Analysis of the CaO

Particle size analysis was conducted on the CaO obtained after the calcination of the clam shells. About 100 g of the pulverised clam shell was used and 3.7 g was retained on the 106 µm screen getting a particle size of 96% passing 106 µm.

A 63 μm screen was also used and 17.1 g was retained, obtaining a particle size of 82.9% passing 63 μm .

2.5 Preparation of Sample Solutions of Waste-acid from Car Batteries

The waste-acid from batteries was obtained from Auto-Electricians that replace the electrolyte (i.e. sulphuric acid) in car batteries in the Tarkwa Nsuaem Community. More than 3–5 litres of waste-acid is generated and discarded on daily basis by each technician in the community. Five (5) litres of waste acid (Fig. 4) was obtained and the specific gravity checked using a hydrometer.



Fig. 4 Waste Battery Acid obtained in the Raw Form

Specific gravity of 1.25 g/cm^3 was recorded indicating a very high concentration of the acid. 250 ml of the 18.75 M Sulphuric acid was diluted to 4.5 M, 5 M, 5.5 M, 6 M, 6.5 M concentrations (Fig. 5) for the reaction of the pulverised clam shells into calcium sulphate.



Fig. 5 Samples of Five Concentrations of WBA used for the Experiment

Atomic absorption spectrophotometric analysis (AAS) was done on the waste battery acid obtained to check the lead content in order to ascertain its

harmfulness to the environment when wrongfully disposed. A substantial amount of 1.0503 mg/L of lead (Pb) was recorded in the 4.5 M concentration of the WBA; the stock WBA contains 4.167 mg/L of lead (Pb).

2.6 Reaction of the Pulverised Clam Shells with Sulphuric acid

About 100 g of the pulverised clam shells were reacted with the various concentrations of sulphuric acid prepared. The reaction is exothermic and thus was monitored with a Digital 2 k-type Thermocouple Thermometer (Nicety DT804A) to determine the time taken for the reaction to be completed and also the maximum temperature at which the reaction was completed. The solution was then filtered and the pH of the filtrate was recorded.

2.7 Drying and Analysis of the Residue

The residue after the reaction was oven dried for 48 hours at temperatures around 130 $^{\circ}\text{C}$ and the dried residue (Fig. 6) was weighed. A representative sample of the dried residue was taken for XRD analysis.

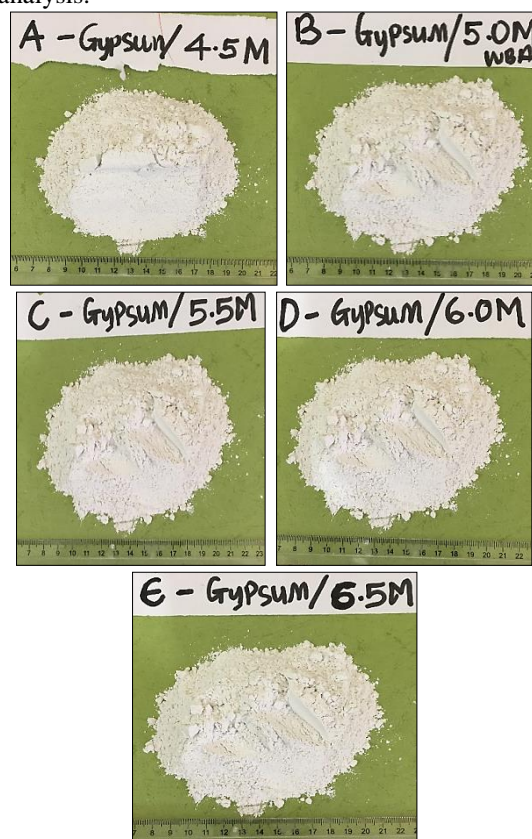


Fig. 6 Dried Residue of the Respective Concentrations WBA used

3 Results and Discussion

3.1 Calcination of Clamshells

The calcination of CaCO_3 and the Gibbs free energy change that accompanies the calcination process are illustrated below (Gilchrist, 1989):



$$\Delta G_r^\circ = 177,100 - 158T \quad (J/mol) \quad (2)$$

From equation (2), the equilibrium temperature for the calcination of pure CaCO_3 is about 848 °C, suggesting that temperatures in excess of about 900 °C should be sufficient for the process. Complete calcination of pure CaCO_3 is accompanied by a weight loss of about 43.97% that stoichiometrically corresponds to complete expulsion of CO_2 gas.

Since the clamshells were given sufficient time to dry, the percent calcination was calculated based on the maximum weight loss attributed to CO_2 and was expressed by equation (3) as follows:

$$\% \text{ Calcination} = \frac{\% \text{ weight loss}}{43.97} \times 100 \quad (3)$$

Fig. 7 shows the percent calcination and the percentage weight loss associated with the calcination of the clam shells. It is clear that the weight loss ranged from about 41.32% to about 43.20% with an average of 41.92%. This gives an average percent calcination of about 95.33%, with a range of 93.97 – 98.25%, suggesting that calcination is incomplete. However, eqn. (3) is based on 100% CaCO_3 purity, which cannot be said to be the case of the clam shells used for the investigation. This is explained further under Section 3.5.

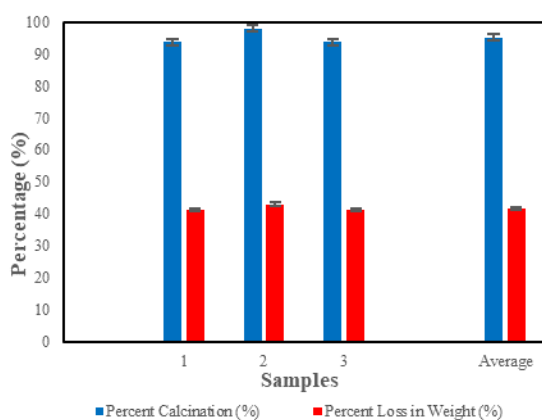


Fig. 7 Graph of Percent Weight Loss after Calcination

3.2 Volume of Waste Battery Acid used for Reaction Analysis

About 100 grams of the pulverised clam shells were used for the reaction against five labelled samples A, B, C, D and E of concentrations 4.5 M, 5 M, 5.5 M, 6 M, and 6.5 M respectively.

The reaction for the formation of calcium sulphate is given by equation (4):

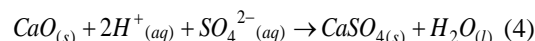


Fig. 8 shows the concentration and the corresponding volume of the acid used. Since the $\text{CaO}:\text{CaSO}_4$ molar ratio is 1 and 100 g of CaO was used as the control mass for the reaction, the maximum amount of CaSO_4 that can be produced is 1.783 mol. Concentration is inversely proportional to the volume, and thus the higher the concentration of the acid used for the reaction the lower the volume of acid required to react with CaO . For sample A with concentration 4.5 M, 397 ml of WBA was used for the reaction; the volume of the acid decreases as the WBA concentration increases. Sample E of concentration 6.5 M required 274 ml of the WBA for complete reaction. The gypsum produced is dependent on the availability of the WBA in excess. Sample E however, had limited acid for the reaction. The bed volume was very high due to a larger mass of PCS and small volume of WBA.

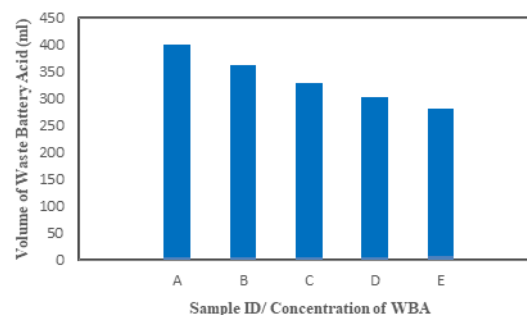


Fig. 8 Volume of Waste Battery Acid Used for the Reaction

3.3 Reaction Time and Temperature Analysis

Fig. 9 shows the maximum temperature difference that accompanies the $\text{CaO}-\text{H}_2\text{SO}_4$ reaction and the time taken for the reaction to reach completion. The release of heat into the environment or surroundings results in the overall negative quantity for the heat of reaction ($\Delta H_{\text{rxn}} < 0$).

The reaction between the pulverised clam shell, which is predominantly calcium oxide (CaO) and

the waste battery acid (WBA) was very exothermic because the temperature of the system increased after the reaction. As shown in Fig. 9, higher acid concentrations gave shorter time for the system to attain their maximum temperature. The samples with low acid concentrations required longer reaction times. Samples D and E took 7 minutes for the reaction to attain its highest temperature difference of 69 °C and 71.2 °C respectively. The observed high temperatures were as a result of higher concentrations of the WBA used.

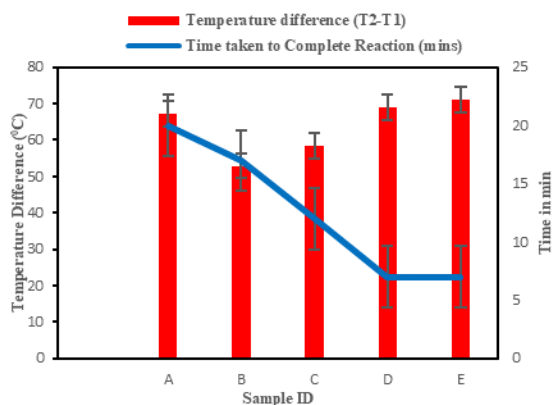


Fig. 9 Graph of Sample ID against Temperature and Time

3.4 Analysis of the Dried Residue and the pH of Filtrate

After the reaction has reached completion, the solution was filtered, and the solid residue dried; the pH of the filtrate was then determined. The initial pH of the Waste Battery Acid before the dilution to be used for the reaction was -1.04 which shows a hydrogen concentration of more than 1 M. From eqn. (1), the molar ratio involved in the reaction is 1:1. Accordingly, a mole of CaO will react with a mole of WBA.

The reaction of a metal oxide with an acid produces water and a metal salt; when calcium oxide reacts with sulphuric acid it produces bubbles of water vapour. After the reaction the pH of the various filtrates obtained were checked along with the masses of dried product obtained at various pH. The highly concentrated H₂SO₄ that was used for the reaction was neutralised in the process. The masses of dried product obtained at various pH of the filtrate are shown in Fig 10. As shown in Fig. 10, the pH of the filtrates was in the range 11.5 – 12.5.



Fig. 10 Graph of Sample ID against the Dried Mass of Residue and pH of Filtrate

Experimentally, assuming 100% purity of the CaO, 56 g of CaO must produce 136 g of CaSO₄. The reaction of the pulverised clam shells with the waste battery acid was based on 100 % purity of the reactants. The dry mass of the residue obtained after the reaction with the pulverised clam shells which was assumed to be 100% CaO gave an average of 134.52 grams of CaSO₄ at the end of the reaction. The masses of CaSO₄ recorded for samples A, B and D were 135.7 g, 135.4 g and 135 g, respectively. The observed slightly lower masses of the calcium sulphate obtained indicate that the pulverised clam shell does not contain 100% CaO or the purity (%H₂SO₄) of WBA was lower than what was estimated. This is because the main components of calcined shells are CaO along with low levels of undesirable impurities, such as Na₂O, SrO, RuO₂, Fe₂O₃ and CuO (Nordin, *et al.*, 2015). The mass of the gypsum produced at the end of the reaction is dependent highly on the excess WBA available, the concentration and also the extent of calcination of clam shells.

3.5 XRD Analysis of the Original Clamshells and Dried Residue obtained after the Reaction

The XRD patterns of the dried original clamshells are shown in Fig. 11 which displays sharp peaks of CaCO₃. After the reaction, the residue that was oven dried at temperatures around 130 °C had almost the same colour as the pulverised clam shells. The XRD of the dried mass obtained after the clam shell-WBA reaction is shown in Fig. 12. Sharp peaks of all the three forms of gypsum, namely, anhydrite (CaSO₄), hemihydrate (CaSO₄ · ½H₂O) and dihydrate (CaSO₄ · 2H₂O) are present along with some CaCO₃; this is a clear indication that the calcination of the clam shells is not fully complete and also that SiO₂ is the basic impurity. From the XRD results in Fig. 12, the hemihydrate (CaSO₄ · ½ H₂O) was dominant followed by the anhydrite (CaSO₄) form of gypsum.

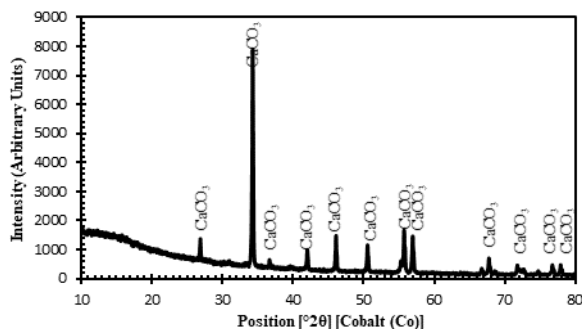


Fig 11 XRD Patterns of Pulverised Clamshells

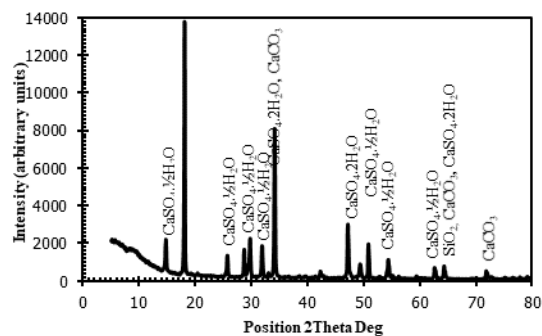


Fig. 12 XRD analysis of Dried Residue obtained from calcined clamshell-WBA interaction

4 Conclusions

This research work investigated the production of gypsum from clam shells and waste battery acid. It was concluded from this research that:

- (i) Clamshells are rich sources of CaCO_3 that can be calcined to produce CaO for subsequent production of gypsum.
- (ii) Various forms of gypsum can be produced from calcined clamshell-WBA interaction.
- (iii) All the three forms of gypsum (Anhydrite, Hemihydrate and the Dihydrate) were produced from the clamshell-WBA interaction.
- (iv) Gypsum production is a potential route for recycling WBA.

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