

# Regeneration of calcium oxide (CaO) from waste gypsum via two-step reaction

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**Abstract**—The regeneration of calcium oxide from gypsum is the interest of this research. Gypsum was converted to calcium oxide via a two-step process involving chemical and thermal reactions. X-ray diffraction (XRD) was used to analyse the samples to identify the samples. Laboratory grade gypsum (LG) and waste gypsum (WG) were used in this research and successful conversion was done. Gypsum was converted into calcium hydroxide by reacting with sodium hydroxide, 0.1 M, solution. Then, calcium hydroxide was calcined, at 700°C, to form calcium oxide. The chemical changes were analysed using X-ray diffraction, wavelength dispersive X-ray fluorescence and thermogravimetric analysis methods.

**Keywords**—gypsum, waste gypsum, calcium hydroxide, calcium oxide

## I. INTRODUCTION

Gypsum is a soft sulphate mineral salt that naturally occurs in the earth's crust. It is composed of calcium sulphate dihydrate and has the chemical formula of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . There is another form of  $\text{CaSO}_4$  mineral known as gypsum anhydrite or anhydrous calcium sulphate with the chemical formula  $\text{CaSO}_4$ . Another form is known as gypsum plaster or plaster of Paris. It has a chemical formula of  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . This study took an interest to regenerate calcium oxide (CaO) from  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , especially, in converting waste gypsum (WG) into CaO. One of the major sources of the WG is as a by-product of the extraction process of titanium (IV) oxide from the ilmenite ores. The total accumulation of WG in Malaysia is between 340,000 tonnes to 400,000 tonnes per year and the major constituent of the WG is hydrated  $\text{CaSO}_4$  at 70 wt.% [1,2]. This causes problems such as storing and environmental pollution. The conventional way and in previous studies, CaO was regenerated from WG via reductive decomposition. This method employs the reduction of WG in a reductive environment with the aid of very temperature ranging from 700°C to 1500°C. Plus, this method tends to evolve sulphur dioxide ( $\text{SO}_2$ ) gas [3-6]. A two-step method eliminates the need of high temperature and the evolution of  $\text{SO}_2$  in the regeneration of CaO from WG. This two-step method involves reacting WG with sodium hydroxide (NaOH). Gypsum converts into calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) in 0.1 M solution of NaOH [7]. Then, the second step involves calcining  $\text{Ca}(\text{OH})_2$  to produce CaO.

## II. EXPERIMENTAL

### A. Materials

The chemical materials used in this study were sodium hydroxide (NaOH), gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) and calcium oxide (CaO). All these chemicals are the products of HmbG Chemicals. Waste gypsum is obtained from Tioxide (M) Sdn. Bhd., Terengganu, Malaysia (manufacturer of titanium dioxide).

### B. Calcium Oxide Regeneration

Laboratory grade gypsum (LG), NaOH and deionised water (DW) were mixed in a beaker in the ratio of 2.15 g to 1 g to  $\leq 250$  mL respectively. The mixture was stirred using magnetic bar for 3 h under room temperature and pressure. The mixture was filtered using filter paper and washed with 100 mL of DW to remove any NaOH residue and the water soluble sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) produced. The collected solid was dried in oven overnight at 110°C. Some dried solid was collected on stage and labelled as S1. The remaining dried solid was calcined in a furnace at from room temperature to 700°C (heating rate 10°C/min) and kept for 2 h at maximum temperature. The calcined solid was collected and labelled as S2.

WG was dried and homogenised into powder. A magnet was used to remove the iron and iron oxide dust from the WG powder. Some powder was collected and labelled as S3. The powdered WG was treated in the same manner as LG was used (assuming WG is consists only of gypsum). The solids collected before (after chemical reaction) and after the calcination were labelled as S4 and S5 respectively.

### C. Analysis

LG, WG, laboratory grade CaO, sample S1, sample S2, sample S3 and sample S5 were analysed using X-ray diffraction (XRD), Rigaku, with  $\text{Cu K}\alpha$  X-ray as a source. Plus, sample S3 was also analysed using wavelength dispersive X-ray fluorescence, WDXRF, (Bruker S8 TIGER). Also, sample S1 and along with sample S4 were analysed via thermogravimetric analysis (TGA), Mettler Toledo TGA instrument, from 25°C to 900°C with 10°C/min heating rate.

## III. RESULTS AND DISCUSSION

## A. XRD Analysis

The diffractogram of LG (Fig. 1a) showed intense diffraction peaks found at  $11.87^\circ$ ,  $20.94^\circ$ ,  $23.63^\circ$ ,  $26.36^\circ$  and  $48.07^\circ$  (2 theta) corresponding to the Miller indices 020, 021, 040, 041 and 260. By comparing the diffractogram of LG and sample S1 (Fig. 1b), it is evident that LG have chemically reacted with NaOH to form  $\text{Ca}(\text{OH})_2$ . Sample S1 showed new intense diffraction peaks found at  $8.13^\circ$ ,  $28.72^\circ$ ,  $34.15^\circ$ ,  $47.18^\circ$ ,  $50.80^\circ$ ,  $54.45^\circ$ ,  $62.66^\circ$ ,  $64.30^\circ$  and  $71.75^\circ$  (2 theta) corresponding to the Miller indices 001, 100, 011, 012, 110, 111, 021, 013 and 022. Again, by comparing the previous two diffractograms with sample S2 (Fig. 1c), it is evident that the  $\text{Ca}(\text{OH})_2$  have dehydrated to form CaO. Sample S2 showed new intense diffraction peaks found at  $32.24^\circ$ ,  $37.40^\circ$ ,  $53.89^\circ$ ,  $64.21^\circ$ ,  $67.45^\circ$  and  $79.76^\circ$  (2 theta) corresponding to the Miller indices 111, 200, 202, 311, 222 and 400. The compound from sample S2 is further confirmed to be CaO by the XRD profile of laboratory grade CaO (Fig. 1d) which matched completely with S2.

The diffractograms of sample S3 (Fig. 2a) and S5 (Fig. 2b) shows a similar trend in the chemical change from the starting material, WG, to end product, CaO, respectively. Sample S3 shows intense diffraction peaks found at  $11.64^\circ$ ,  $20.73^\circ$ ,  $23.39^\circ$ ,  $29.11^\circ$  and  $47.83^\circ$  (2 theta) corresponding to the Miller indices 020, -121, 031, -141 and 062; which are of gypsum. Whereas, sample S5 shows intense diffraction peaks found at  $32.28^\circ$ ,  $37.47^\circ$ ,  $53.94^\circ$ ,  $64.28^\circ$ ,  $67.52^\circ$ ,  $79.85^\circ$  and  $88.64^\circ$  (2 theta) corresponding to the Miller indices 111, 200, 202, 311, 222, 400 and 313; which are of CaO and were absent in the diffractogram of sample S3. The sharp and narrow peaks in all six diffractograms indicate solid crystalline structure of the samples.

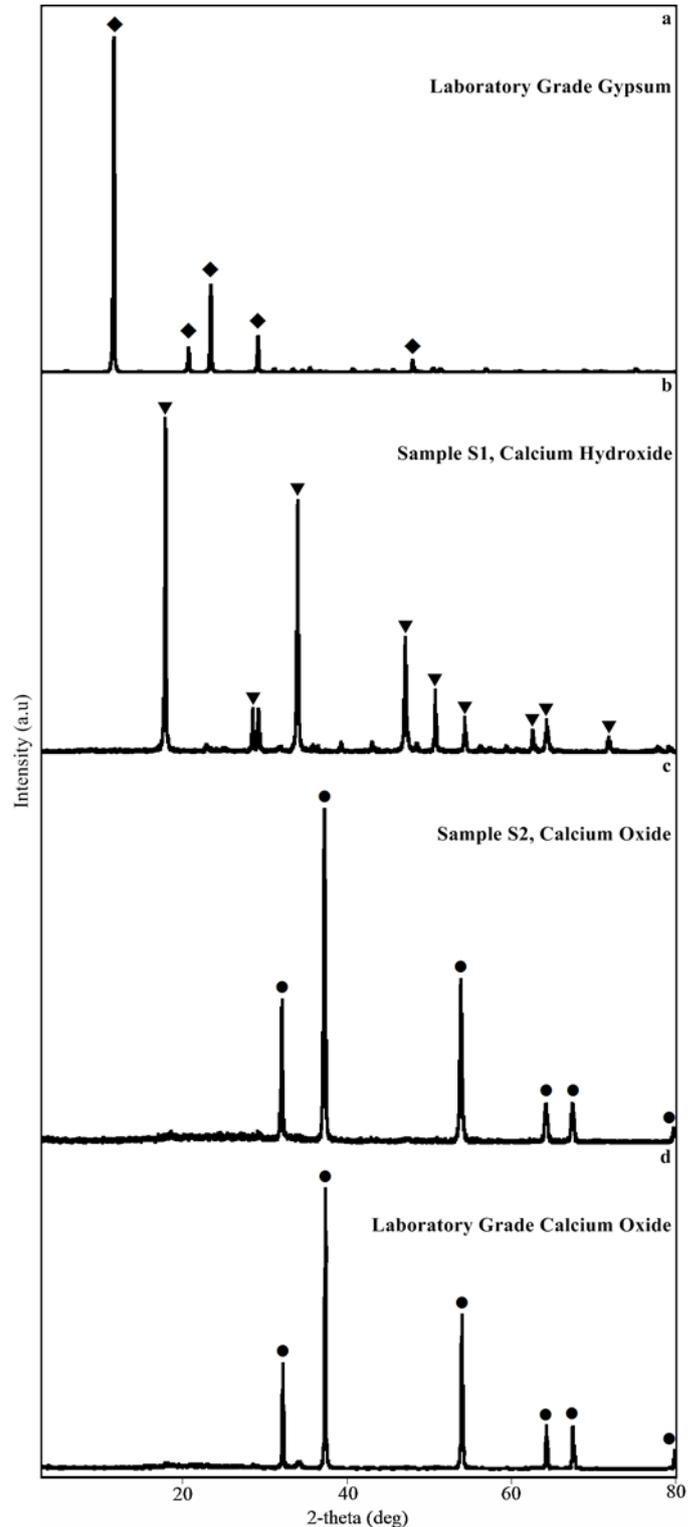


Fig. 1. XRD profiles of LG, sample S1, sample S2 and commercial calcium oxide (♦: gypsum, ▼:  $\text{Ca}(\text{OH})_2$ , ●: CaO).

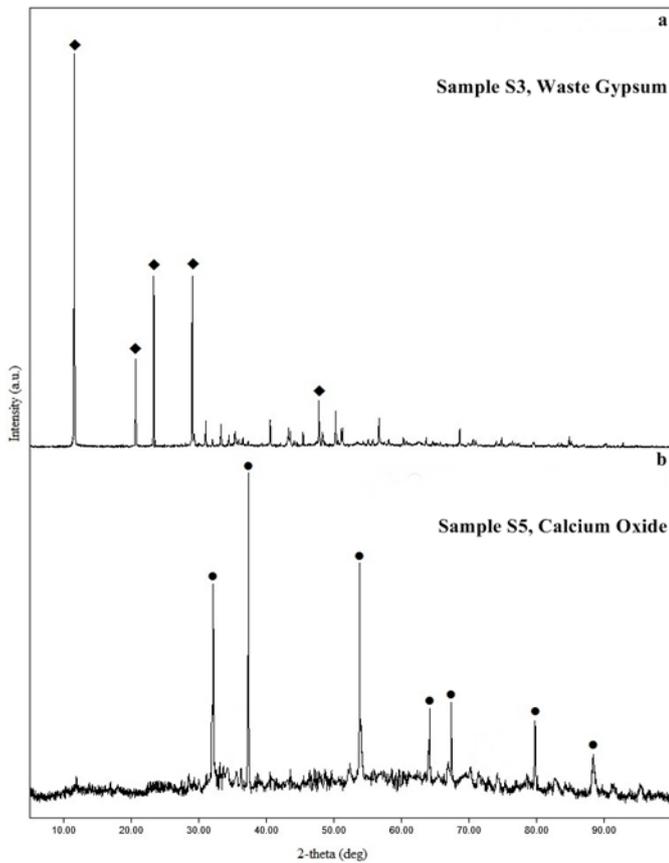


Fig. 2. XRD profile of waste gypsum and calcium oxide from waste gypsum (♦: gypsum, ●: CaO).

**B. XRF Analysis**

The WG obtained is known as red gypsum due to its high content of iron/iron oxide in it. The X-ray fluorescence (XRF) analysis result in Fig. 3 shows the four major compositions (calcium, iron, sulphur and titanium) of WG and their percentages.

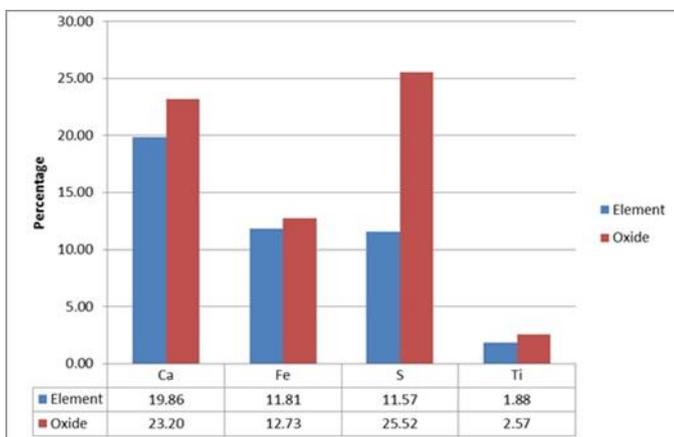


Fig. 3. XRF analysis results of waste gypsum.

**C. Thermogravimetric Analysis**

Thermal decomposition of sample S1,  $\text{Ca(OH)}_2$ , (Fig. 4) occurs in several steps. Firstly the surface water is given off from 100°C to 130°C, a 7.90% mass reduction. Then water from the mineral matrix is released from 410°C to 460°C, a 10.40% mass reduction. And the final stage decomposition takes place at 580°C to 660°C, a 1.59% mass reduction, where calcium hydroxide is completely converted into calcium oxide. Some slight and very gradual of mass reductions (total of 2.17%) were observed in between these steps. The overall mass loss is 22.06%.

The TGA curve of sample S4,  $\text{Ca(OH)}_2$  from WG, (Fig. 5) shows similar trend of decomposition as sample S1. Initially there is a gradual reduction in mass on sample S4 in the temperature range of 25°C to 400°C. Then there is a sudden reduction of mass in a short temperature range of 400°C to 450°C. This first 5.98% and second 9.72% mass reduction might be due to the loss of surface water and matrix water in sample S4 ( $\text{Ca(OH)}_2$ ), respectively. Then again there is a gradual mass loss of 1.83% in the temperature range of 450°C to 600°C. Finally, the last sudden mass loss occurred in the temperature range of 600°C to 700°C where the final mass percentage was 78.79%. At this range the  $\text{Ca(OH)}_2$  has totally converted into CaO. The overall mass loss is 21.21%. The slight lowering in total mass loss of both sample S1 and sample S4 is might be due to the presence of impurities. Thus, it is decided that the best temperature for calcining  $\text{Ca(OH)}_2$  is 700°C.

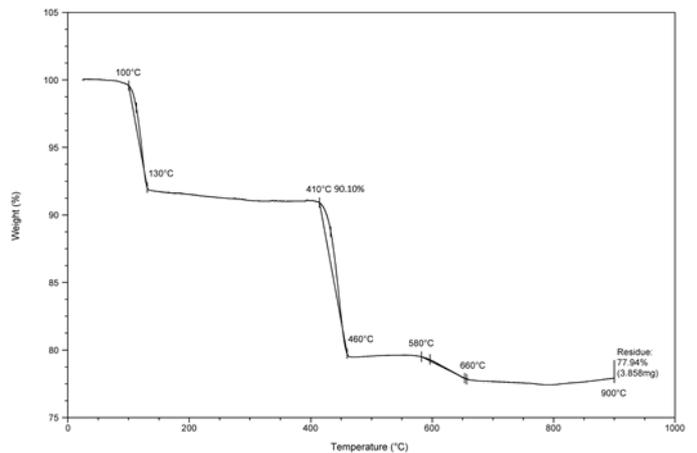


Fig. 4. TGA thermograph of sample S1 (thermal decomposition of  $\text{Ca(OH)}_2$  from LG).

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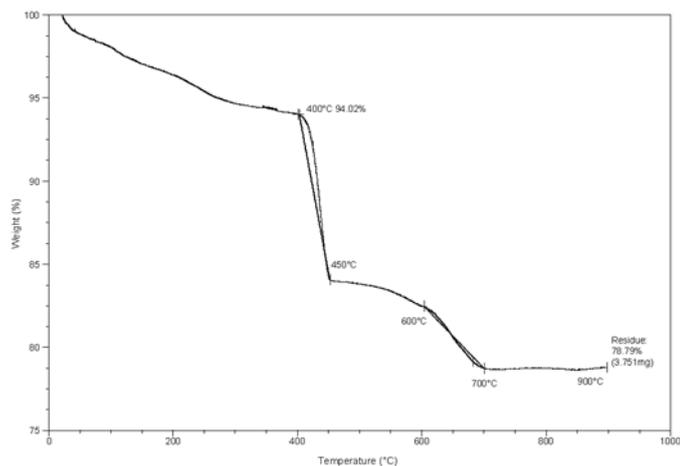


Fig. 5. TGA thermograph of sample S2 (thermal decomposition of Ca(OH)<sub>2</sub> from WG).

## IV. CONCLUSION

The regeneration of CaO from WG via a two-step method is proven to be effective in using lower thermal energy, at 700°C, and being environmentally friendly by eliminating the evolution of SO<sub>2</sub> gas. The traditional method would have the danger in evolving this harmful gas, whereas the sulphate ion in gypsum was successfully transferred to the sodium ion and forming Na<sub>2</sub>SO<sub>4</sub>.