



High temperature CO₂ sorption using Ca(OH)₂ in pilot scale packed column

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ABSTRACT

Carbon dioxide is the major content of greenhouse gases, which is released by many industries such as paper, cement and steel industries etc. Removal or separation of CO₂ from the atmosphere is a challenging task for the researchers as it related to the human health and affects environment. Many methods and techniques have been tried for the removal of CO₂, among them sorption method was found to be more simple and economical. Majority of research work related to CO₂ sequestration was carried out using Thermo Gravimetric Analysis (TGA). In the present study an attempt was made to study high temperature CO₂ sorption using self-fabricated packed bed column in pilot scale. In this work the absorption column was designed to utilize the flue gas temperature for effective sorption of carbon dioxide using Calcium hydroxide [Ca(OH)₂] as a sorbent. The Ca(OH)₂ was made into cylindrical extrudates. The gas mixture containing nitrogen and carbon dioxide was heated and subjected to CO₂ sorption using Ca(OH)₂. The sorption process for various temperatures was studied at a constant flow rate and fixed bed height. Concentration of CO₂ was measured using a flue gas analyzer (NDIR sensors). The temperature was found to be major factor affecting sorption process. The optimum temperature was found to be 300 °C. Increase in the temperature above 300 °C, resulted in sintering and weight loss of the sorbent. The conversion of Ca(OH)₂ to CaCO₃ is confirmed by FT-IR, Scanning Electron Microscopy (SEM), Energy Dispersive X-Ray Analysis (EDAX) and XRD.

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1. Introduction

Global warming is a major concern in 21st century, which is resulted from the greenhouse gases released by various industries. Greenhouse gases mainly consists of CO₂, which is a by-product of many industries such as steam forming of hydrocarbons, paper, cement, steel industries. CO₂ is considered as the major content of greenhouse gases [1,2]. Removal or separation of large quantity of CO₂ released by industries is inevitable. Many methods are employed to separate CO₂ from entering into atmosphere, but sorption method [3] was found to be more economical and simplest [4]. Zeolites, persovskites, hydrotalicates, soda lime, polymeric membranes, fcu-MOF based rare-earth metals and also metal oxides like lithium zirconates, lithium potassium zirconates, sodium metasilicates, etc., are used as a sorbents to capture or separate CO₂ from the atmosphere [5-8]. Usually the metal oxides used as adsorbents for the removal of CO₂ from the flue gas and atmosphere, forms respective solid metal carbonates [9-11]. Normally, physical and chemical decay of sorbent will takes place in any gasifier system, so it is better to replenish the sorbent after few runs or use of low cost sorbent is advisable [4].

CaO is considered as sorbent for CO₂ removal because it is economic and abundant, which can be obtained from precursors like limestone, dolomite and calcium hydroxide by heating above its calcination temperature [4,12]. CO₂ capture by solid CaO for industrial application is well known. DuMotay and Marechal used lime to enhance the gasification of carbon with steam [13]. Curran *et al.* showed CO₂ acceptor process for the gasification of lignite coal to produce H₂ rich gas [14]. The synthesis of calcium cyanamide was also carried out by using the reaction between CaO and CO₂ [14]. Later, CaO was used to separate CO₂ from coal-combustion flue gas [14-18]. More recently, CaO is used as a CO₂ capture for zero-emission coal technology and HyPr-RING process [4,19] in novel coal gasification.

The conversion of calcium hydroxide to calcium carbonate is faster compare to calcium oxide to calcium carbonate [20]. The efficiency of Ca-based sorbents for CO₂ sorption decreases with increase in number of cycles at atmospheric and pressurized conditions, because of sintering with carbonation-regeneration cycle at high temperature [21,22].

Matsuyama *et al.*, have stated that the temperature should be below 200 °C during separation of CO₂ [23].

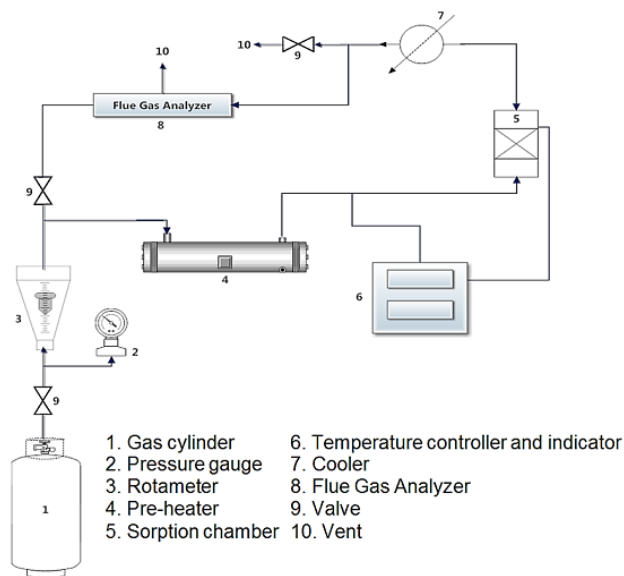
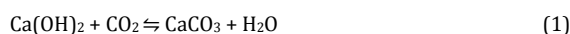


Figure 1. Schematic diagram of experimental setup.

But, this is impossible in case of thermal plants where CO₂ capture or separation should take place at high temperature [24]. Majority of research work related to CO₂ sequestration or capture was done by Thermo Gravimetric Analysis-Differential Thermal analysis (TGA-DTA) [4,25,26]. In the present work, an attempt was made to improve the sorption percentage of CO₂ in a pilot scale [27] with less error and simple standardized procedure. In this study, the CO₂ capture was studied in pilot scale, using Ca(OH)₂ extrudates in packed bed column using self-fabricated high temperature sorption system. The most probable reaction of Ca(OH)₂ with CO₂ is represented in Equation 1. The Equation (1) is reversed at a particular temperature, because the partial pressure of CO₂ in the product gas is lower compared to the equilibrium partial pressure of CO₂ [4].



In the present work, the effect of temperature on sorption in pilot scale was studied. The optimum temperature of the reaction was estimated and the break through curves at varied temperatures at sorbent bed height of 2.5 cm. The conversion of Ca(OH)₂ was confirmed by Fourier transform infrared (FT-IR), X-ray Diffraction (XRD), Energy dispersive X-ray analysis (EDAX) and Scanning electron microscopy (SEM) analysis. The sintering temperature of Ca(OH)₂ was also estimated.

2. Experimental

2.1. Materials

Calcium hydroxide (Ca(OH)₂, 96% GR) was procured from Merck chemicals. Calcium hydroxide powder is made into extrudates by using extrudator fabricated by M/S Deepthi Engineering, Bangalore.

2.2. High temperature CO₂ sorption system

A pilot scale high temperature CO₂ sorption experimental setup was designed, and the sketch of the sorption equipment is shown in Figure 1. The equipment was fabricated by M/S Deepthi Engineering, Bangalore. High temperature sorption system consists of gas cylinder, heating system, absorption

chamber and flue gas analyzer equipment. The gas cylinder was consisting of 85% N₂ and 15% CO₂, which is similar to that of flue gas/stack gas from the industries. The heating system was designed in such a way that the gas temperature and bed temperature was maintained constant during the study. The analyzer is made of NDIR (Non-Dispersive Infra-Red) and electrochemical sensors with filter and moisture absorption system to measure CO₂ and traces of oxygen and hydrocarbons continuously from flue gas. Calcium hydroxide was used as sorbent which is made into extrudates using self-designed manual extrudator. The extrudates are average of 12 mm length and 1.5 mm diameter. The extrudates were dried at 110 °C to remove the moisture before using in the packed column. The height of the sorbent packing was maintained 5 cm in a sorption column of 3.9 cm diameter. The mass of the sorbent for 5 cm packing was 28±5 g. The heating system was designed in such way that the temperature can be varied from 100 °C to 1000 °C using copper tubes with band heaters (2 kW). The calibrated rotameter was fixed at the entry to measure gas flow rate before entering the system. The outlet gas from the absorption chamber was cooled using a heat exchanger. The composition of inlet and outlet gas was measured using a flue gas analyzer. Prior to passing the gases to absorption and heating chamber, the heaters were switched on 40 min in advance to maintain the constant temperature. All the experiments were performed under steady state conditions.

2.3. Characterization methods

Calcium hydroxide before and after sorption studies were characterized by using XRD, SEM, EDAX and FTIR. The crystallinity and morphology of sorbent was determined by using X-ray diffraction (XRD) (Bruker D2 Phaser, USA) at 2θ, 5-60 ° with a step size of 0.02 ° per 0.5 sec. Surface morphology and percentage purity of the sorbent before and after sorption was studied using Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray Analysis (EDAX) (FEI-Netherlands-QUANTA200-ESEM). The identification of functional groups of the sorbent before and after sorption was carried out using FTIR (Bruker, USA).

3. Results and discussions

3.1. Sorption studies

3.1.1. Effect of temperature on sorption of CO₂ using column studies for Ca(OH)₂

The sorption experiment was carried out at different temperatures of 100, 150, 300, 500 and 600 °C. Gas flow rate of 30 mL/h was maintained constants. The CO₂ concentration was measured at regular intervals before and after sorption. Inlet CO₂ concentration is 'C₀' and outlet concentration of CO₂ is 'C'. Sorption isotherms are obtained by the column studies. The ratio of outlet to inlet concentration (C/C₀) is plotted against time for different thermal runs as shown in Figure 2. The small amount of CO₂ escapes from the initial contact layer and then removed by the upper strata of the bed. The primary zone, move upwards from saturated adsorbent zone towards the region fresh adsorbent in the column. The flue gas enters into the absorption column first reacts with the surface of Ca(OH)₂ sorbent and forms primary sorption zone. The sorption zone shifts slowly upwards as the flow of CO₂ takes places continuously [28]. As the sorption zone moves upwards more and more CO₂ tends to escape. The ratio C/C₀ increases as the zone move upwards. The breakthrough curve exhibit a characteristic 'S' shape curve with varying degree of steepness. The increase in the temperature from 100 to 300 °C results in the increase in sorption. At 300 °C, the zone movement is very slow and the bed saturation time is very large. It can be concluded that there is a maximum conversion of Ca(OH)₂ to CaCO₃ at 300 °C. The increase in the temperature of the sorption zone above 350 °C, resulted in abrupt analyzer reading. At this temperature, the material undergoes sintering and results in weight loss and decrease in the bed height. At this temperature, the sintered material results in deposition of vaporized impurities in the solenoid valve and air filter of the analyzer [4,24,29]. The deposition of white substance i.e. sorbent material in the air filter blocks the flue gas moment which resulted in abrupt CO₂ concentrations. The weight loss with increase in the temperature may be attributed to the reversibility of the reaction.

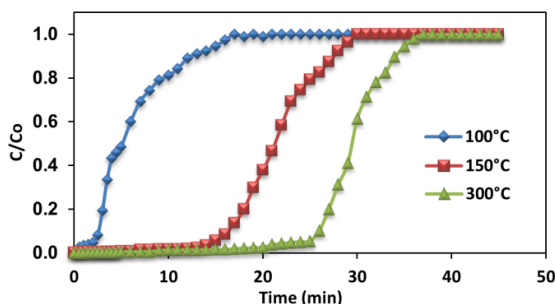


Figure 2. Plot of C/C₀ versus time for CO₂ sorption in Ca(OH)₂.

3.1.2. Effect of temperature on weight change of Ca(OH)₂

The effect of temperature on sorbent weight has been studied to final conversion. The plot of weight percentage with temperatures resulted in bell shaped curve, as shown in Figure 3. Initially with increase in temperature, weight percentage of sorbent increases and attains maximum increase of 10.92% at 300 °C. On increase in temperature above 300 °C, the weight percentage of sorbent decreases resulting in weight loss of the sorbent. This may be attributed to sintering of the sorbent. Sintering results in the decrease of pore size, pore shape, grain growth and change in density due to molecular defects in the sorbent bed [30,31]. At high temperature, the reaction is reversible i.e. Ca(OH)₂ and CO₂ are formed from Ca₂(CO)₃.

Another reason may be due to the conversion of Ca(OH)₂ to CaO and H₂O which takes place at 512 °C where the partial pressure of water in Ca(OH)₂ reaches 101 kPa and hence water vaporizes leaving out CaO. It must be noted that even with such weight loss there may be a conversion of CaO to CaCO₃ [4,20]. The conversion of Ca(OH)₂ to CaCO₃ takes places at faster rate compared to CaO to CaCO₃ [20].

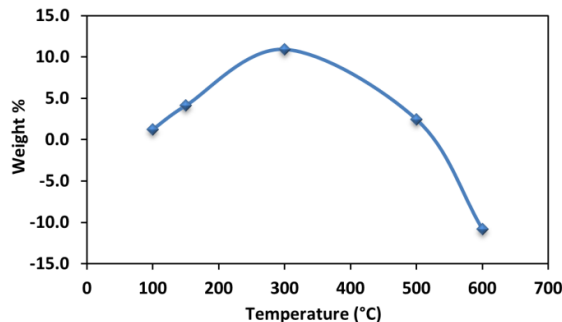


Figure 3. Plot of sorbent weight percentage versus temperature for Ca(OH)₂.

3.1.3. Effect of temperature on percentage conversion of Ca(OH)₂

The change in weight of the sorbent before and after sorption experiment was noted. Conversion of calcium hydroxide to calcium carbonate in presence of CO₂ at different temperatures was shown in Equation 1, which is a reversible reaction. The change in weight of sorbent was noted for experiments conducted at different temperature and percentage conversion was also calculated based on stoichiometry. The percentage conversion of Ca(OH)₂ was plotted against temperature as shown in Figure 4. The resultant graph or pattern was a bell shaped curve with maximum conversion shown at 300 °C. Weight loss observed at high temperatures because of the sorbent sintering. Below 300 °C, the conversion rate of Ca(OH)₂ to CaCO₃ is diffusion-controlled, but above 300 °C, it was chemically controlled [20]. Above the 300 °C temperature, it cannot be concluded that there is no conversion of the sorbent. Nikulshina *et al.*, [20] reported that there is a drastic change in the CO₂ capture from Ca(OH)₂ in Thermo Gravimetric curve (TGC) between 250 to 300 °C temperature, as the temperature increases the CO₂ capture increases. In the present work, the conversion increases with increase in temperature till 300 °C. Above 300 °C, resulted in sintering of the sorbent, this may be due to the creation of hot zones in the packed bed. Whereas, in TGA studies, the solids are entirely covered by the gas, which results in good conversion even at high temperatures.

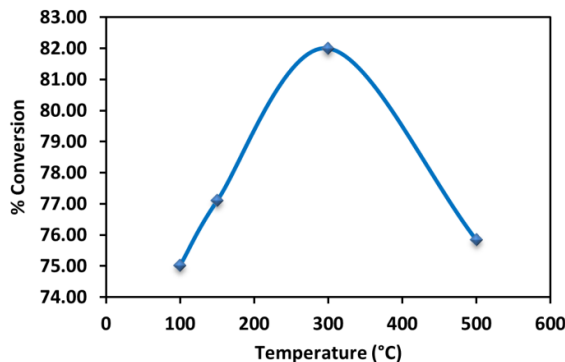


Figure 4. Plot of percentage conversion of Ca(OH)₂ versus temperature.

3.2. Characterization

3.2.1. Scanning electron microscopy (SEM) analysis

The surface morphology of $\text{Ca}(\text{OH})_2$ sorbents before and after CO_2 sorption were characterized by SEM (magnification 10000 \times) as shown in Figure 5 and 6. In Figure 5, $\text{Ca}(\text{OH})_2$ shows uniform surface area. However in Figure 6, the surface of the sorbent is completely covered by lumps represents the reaction of CO_2 with $\text{Ca}(\text{OH})_2$ to CaCO_3 . CO_2 reacts with sorbent at a particular temperature results in the formation CaCO_3 . Figure 6, is the SEM image of CaCO_3 , the lump formation conforms the conversion of $\text{Ca}(\text{OH})_2$ into CaCO_3 .

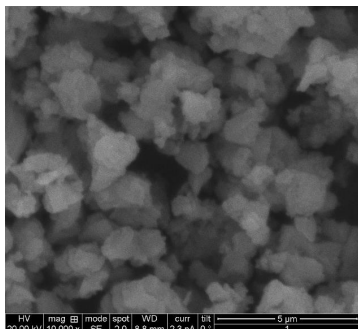


Figure 5. SEM image of $\text{Ca}(\text{OH})_2$.

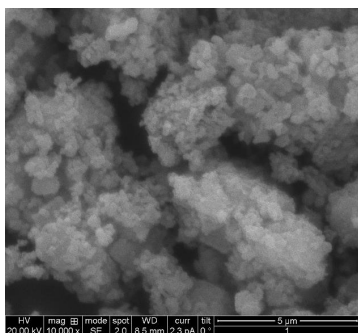


Figure 6. SEM image of CO_2 sorbed $\text{Ca}(\text{OH})_2$.

3.2.2. Energy dispersive X-ray analysis (EDAX)

The purity of the sorbent before and after CO_2 sorption was determined by EDAX analysis, as shown in Figure 7 and 8. From Figure 7, the peaks obtained between 3.5 to 4 KeV corresponds to calcium, the peak obtained near 0.5 KeV represents oxygen and the smaller peak in the region less than 0.4 KeV for carbon. The percentage purity of the sorbent containing Ca, O and C was found to be 62.62, 30.42 and 5.23, respectively. From Figure 8, the peaks obtained for Ca was less intense compare to Figure 7, but the peaks for O and C more intense. The purity of the sorbent after CO_2 sorption was found to be 57.04, 30.88 and 9.02% for Ca, O and C, respectively, conforms the conversion of $\text{Ca}(\text{OH})_2$ into CaCO_3 in presence of CO_2 .

3.2.3. X-ray diffraction (XRD) studies

XRD pattern of calcium hydroxide is shown in Figure 9. The calcium hydroxide sorbent was converted into calcium carbonate (CaCO_3) in a certain rate with variable temperatures; the conversion is maximum at 300 $^\circ\text{C}$. XRD pattern of the sorbent after sorption is shown in Figure 10, which exactly matches with the JCPDS data of CaCO_3 [Powder Diffraction File. Card no: 85-1108] [32]. In Figure 9, the peaks found at

angle of incidence 17.99 and 34.05 $^\circ$ have more intensity and angle of incidence at 28.8 $^\circ$ have less intensity, whereas in case of Figure 10, the intensity of the peaks are vice versa with some small shifting in peaks. In Figure 10, some additional peaks are obtained at 2θ of 34.19, 39.46, 43.16 and 48.55 $^\circ$ which indicates the formation of rhombohedral CaCO_3 and confirms the capture of CO_2 by $\text{Ca}(\text{OH})_2$ sorbent.

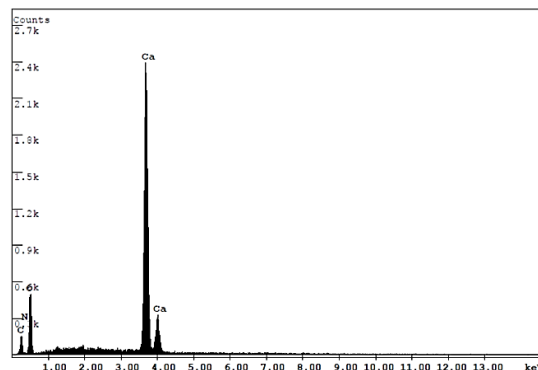


Figure 7. EDAX pattern of $\text{Ca}(\text{OH})_2$.

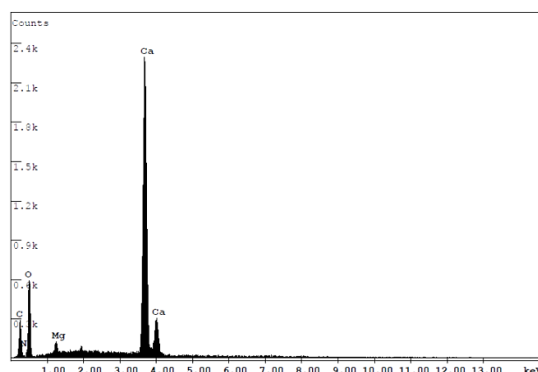


Figure 8. EDAX pattern of CO_2 sorbed $\text{Ca}(\text{OH})_2$.

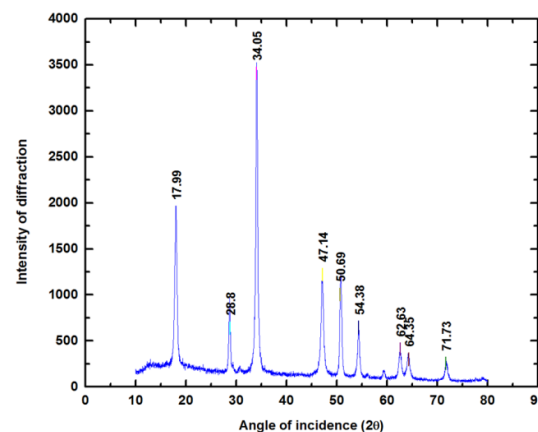


Figure 9. XRD pattern of $\text{Ca}(\text{OH})_2$.

3.2.4. Fourier transform infrared (FT-IR) studies

Figures 11 and 12 represents FT-IR spectrum of pure $\text{Ca}(\text{OH})_2$ and $\text{Ca}(\text{OH})_2$ after CO_2 sorption, respectively. In FT-IR spectra of pure $\text{Ca}(\text{OH})_2$, peak at 1419.51 cm^{-1} indicates the presence of -OH functional group. These functional groups at

the surface are the adsorbing sites of the metal oxides. FT-IR spectra of adsorbed material show changes in terms of peak shifts. The extra peaks noticed at 2357 and 2513 cm^{-1} indicates asymmetric stretching of CO_2 molecules. The positive shift is observed in the peaks which may be due to interaction of CO_2 with functional groups. Some more additional peaks were observed at 1400 and 1447 cm^{-1} , which may be also due to symmetric vibrational mode of bicarbonates. The peaks obtained at 715, 878 and 1430 cm^{-1} confirm the formation carbonate and these attributes to the vibration of carbon-oxygen double bond in carbonate ion. These peak shifts may be due to strong interactions of CO_2 in carbonates and bicarbonates with hydroxyl groups attached to the metal hydroxide. Larger peak shifts were observed in the adsorbed material than the spectra of pure material, this clearly indicates greater CO_2 sorption [33].

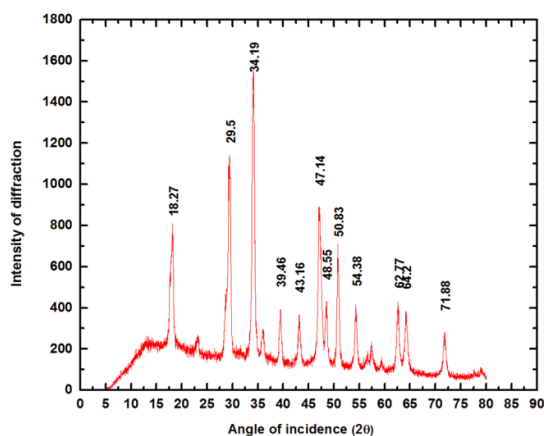


Figure 10. XRD pattern of CO_2 sorbed Ca(OH)_2 .

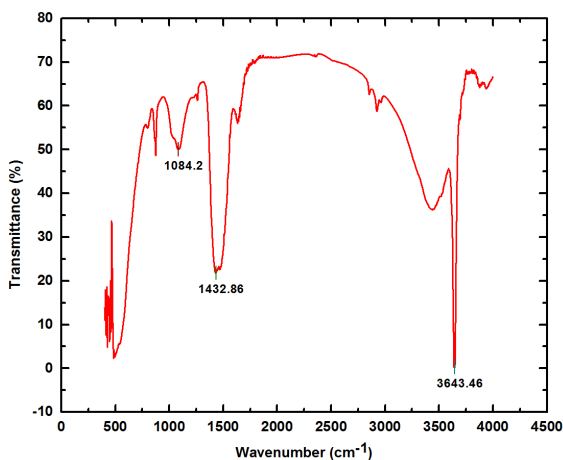


Figure 11. FT-IR spectrum of Ca(OH)_2 .

4. Conclusions

The sorption experiments were carried out using calcium hydroxide as sorbent by varying temperature from 100 to 600 $^{\circ}\text{C}$ in self-fabricated sorption system. At 300 $^{\circ}\text{C}$, the plot of C/C_0 (ratio of outlet to inlet concentration) vs time graph takes more time for stabilization compared to others graphs at different temperatures. Hence, 300 $^{\circ}\text{C}$ is the optimum temperature, where maximum weight percentage and percentage conversion of the sorbent was found to be 11 and 82%, respectively. Above 500 $^{\circ}\text{C}$, both the sorbent weight

percentage and percentage conversion decreases because of sintering. The sorption of CO_2 by Ca(OH)_2 was also confirmed by SEM, XRD and FT-IR analysis.

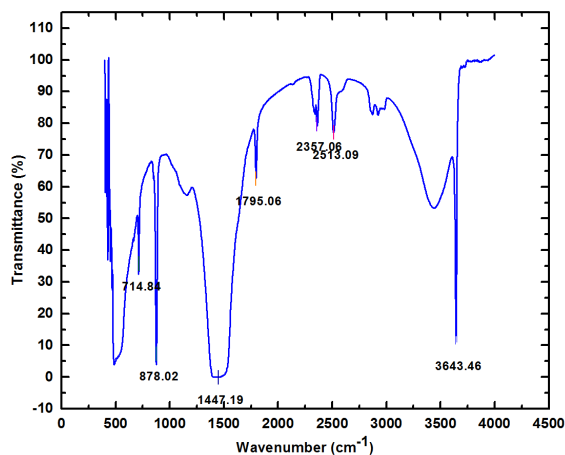


Figure 12. FT-IR spectrum of CO_2 sorbed Ca(OH)_2 .

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