

## Article

# Effect of the Presence of HCl on Simultaneous CO<sub>2</sub> Capture and Contaminants Removal from Simulated Biomass Gasification Producer Gas by CaO-Fe<sub>2</sub>O<sub>3</sub> Sorbent in Calcium Looping Cycles

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**Abstract:** This study investigated the effect of HCl in biomass gasification producer gas on the CO<sub>2</sub> capture efficiency and contaminants removal efficiency by CaO-Fe<sub>2</sub>O<sub>3</sub> based sorbent material in the calcium looping process. Experiments were conducted in a fixed bed reactor to capture CO<sub>2</sub> from the producer gas with the combined contaminants of HCl at 200 ppmv, H<sub>2</sub>S at 230 ppmv, and NH<sub>3</sub> at 2300 ppmv. The results show that with presence of HCl in the feeding gas, sorbent reactivity for CO<sub>2</sub> capture and contaminants removal was enhanced. The maximum CO<sub>2</sub> capture was achieved at carbonation temperatures of 680 °C, with efficiencies of 93%, 92%, and 87%, respectively, for three carbonation-calcination cycles. At this carbonation temperature, the average contaminant removal efficiencies were 92.7% for HCl, 99% for NH<sub>3</sub>, and 94.7% for H<sub>2</sub>S. The outlet contaminant concentrations during the calcination process were also examined which is useful for CO<sub>2</sub> reuse. The pore structure change of the used sorbent material suggests that the HCl in the feeding gas contributes to high CO<sub>2</sub> capture efficiency and contaminants removal simultaneously.

**Keywords:** CO<sub>2</sub> capture; contaminant removal; CaO-Fe<sub>2</sub>O<sub>3</sub> sorbent; calcium looping

## 1. Introduction

A growing need to reduce carbon dioxide (CO<sub>2</sub>) emissions has led to development of new materials and processes for effective, economical, and reliable carbon capture. The low costs and readily availability of Ca-based material makes the calcium-looping (CaL) process very promising for CO<sub>2</sub> capture from combustion flue gas and gasification producer gas [1–4]. Recently, the calcium looping technology has been studied to improve the producer gas quality and increase the producer gas energy content when the CO<sub>2</sub> sorbent material is applied to the biomass gasification process [5–7].

The calcium looping process consists of two reversible reactions among CaO, CO<sub>2</sub>, and CaCO<sub>3</sub> by changing the operation temperatures and alternatively switching gas streams [8,9]. In the forward reaction, termed as carbonation, CaO reacts with CO<sub>2</sub> to form CaCO<sub>3</sub> which, in turn, decomposes to CaO and CO<sub>2</sub> in the reversal reaction, termed as calcination. The producer gas from steam biomass gasification mainly consists of H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub> [2,3]. However, there are impurities in the producer gas including ammonia (NH<sub>3</sub>), hydrogen sulphide (H<sub>2</sub>S), and hydrogen chloride (HCl) converted from the N-based, S-based, and Cl-based species in the feedstock [5,10–12]. The concentrations of the above-mentioned

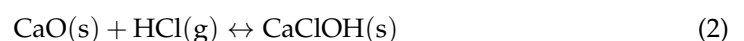
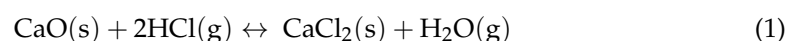
contaminants in the steam biomass gasification producer gas are, respectively, 200 ppmv for HCl, 230 ppmv for H<sub>2</sub>S, and 2300 ppmv from NH<sub>3</sub> [12–18].

Many studies have demonstrated that the reactivity and recyclability of the calcium-based sorbent are crucial factors in the economic viability of the CaL [19]. Most of Ca-based materials exhibit continuous deactivation in presence of gaseous contaminants and cyclic operation [20–24]. In addition, attrition is another issue for natural calcium material such as limestone. Therefore, various methods have been developed to enhance CO<sub>2</sub> capture durability by enhancing the active surface area and porosity of the sorbent material. One of these methods involves incorporating metal oxide into the sorbent material [25–27] as implemented in developing the novel sorbent material which has been used in this study [28]. Addition of Fe<sub>2</sub>O<sub>3</sub> in the CaO based sorbent can enhance the integrity and lasting activity of sorbent material during calcium looping process, which facilitates the CO<sub>2</sub> capture and provides catalytic effects on contaminant removal. This synthetic sorbent material is promising aspect of cyclic stability and strength over multiple carbonation-calcination cycles, while keeping the surface area available and active during carbonation [28]. It should be noted that Fe<sub>2</sub>O<sub>3</sub> in the sorbent material decreased the heat demand for the endothermic calcination process resulting the cost reduction in calcium looping process. Thus, improving CO<sub>2</sub> capture performance with simple and inexpensive methods is important.

An alternative strategy was also proposed by modification of the sorbent material using organic and mineral acids thus to increase its capture capacity [29]. In this way, HCl may be a suitable acid to improve the CO<sub>2</sub> capture performance of the Ca-based sorbent material. However, few studies have examined the effect of chlorine in biomass gasification producer gas on CO<sub>2</sub> capture performance of Ca-based material under carbonation and calcination looping, therefore further research and analysis are needed.

Our previous studies have demonstrated that the carbonation temperature is a key parameter affecting the CO<sub>2</sub> capture efficiencies of the sorbent material composed of CaO-Fe<sub>2</sub>O<sub>3</sub>. It was found that the optimum carbonation temperature is between 620 and 680 °C for capturing CO<sub>2</sub> by this sorbent material. In the experiments by Wang et al. [30,31], limestone was used as the sorbent material and mixture of CO<sub>2</sub> and N<sub>2</sub> was used as the testing gas in which the HCl was added as contaminant. From this study it was found that calcium-based sorbent were most effective in capturing CO<sub>2</sub> at temperatures of 650–720 °C. A similar study was reported by Chyang et al. [32] who found that the optimum carbonation temperature for removing HCl by the CaO based material was 650 °C from examining the effect of operating temperature in the range of 600–800 °C. It would be expected that both carbonation and chlorination reactions occur within the sorbent material at the carbonation temperature. Separate studies show that contaminants in the feeding gas may affect the optimum temperature of the carbonation reaction as contaminants can affect the reaction kinetics and the sintering of the sorbent material [33,34].

Studies on effect of HCl on the Ca-based sorbent material confirmed the reaction between HCl and CaO to form CaClOH and, eventually, the end product of CaCl<sub>2</sub> [35–41]. Therefore, adding HCl to the carbonation step results in simultaneous carbonation and chlorination with the possible reactions of:



These studies either used combustion flue gas or inert gas as the feeding gas with HCl as the contaminant. To our best knowledge, there are no reported studies on the effect of HCl in the biomass gasification producer gas on simultaneous CO<sub>2</sub> capture and HCl removal by using a CaO-Fe<sub>2</sub>O<sub>3</sub> sorbent material during the CaL process. The present study's ultimate goal is achieving maximum CO<sub>2</sub> capture and contaminants removal during the carbonation stage. Understanding of the fundamental mechanism of interaction between HCl and CaO is important for developing sorbent formulas and optimising

operation conditions. The adsorption of HCl by the CaO based sorbent is reported to be a reversible process with varying reaction temperatures, therefore, it is possible to desorb HCl and regenerate the sorbent by increasing the temperature through calcination [40]. In this regard, concentrations of the contaminants in the outlet gas streams during calcination were also examined, which is useful for reusing the captured CO<sub>2</sub> in plant nursery greenhouses. Furthermore, the effect of HCl addition on the microstructure of the sorbent material after three carbonation-calcination looping cycles was analysed for understanding of the mechanism of HCl impact on the sorbent material performance.

## 2. Materials and Method

### 2.1. Sorbent Material and Preparation

CaO-Fe<sub>2</sub>O<sub>3</sub> based sorbent material, in the form of composite, was developed and supplied by Hot Lime Labs (HLLs) in New Zealand. This sorbent material is composed of 70 wt% CaO, 20 wt% Fe<sub>2</sub>O<sub>3</sub>, and 10 wt% inorganic binders. The raw materials at pre-set composition were physically mixed and pelletised to the required size of about 5 mm. The fresh sorbent material, once received, was analysed to determine BET surface area, sorption pore volume, and average pore diameter, with values of 1.24 m<sup>2</sup>/g, 0.02 cm<sup>3</sup>/g, and 60.1 nm, respectively. Before the experiments, the as-received sorbent material was pre-heated at 650 °C for 1 h to remove volatiles. After the heat treatment the BET surface area, sorption pore volume, and average pore diameter were re-measured. These values were 1.52 m<sup>2</sup>/g, 0.005 cm<sup>3</sup>/g, and 15.5 nm. Fresh sorbent material had a bulk density of approximately 1000 kg/m<sup>3</sup>.

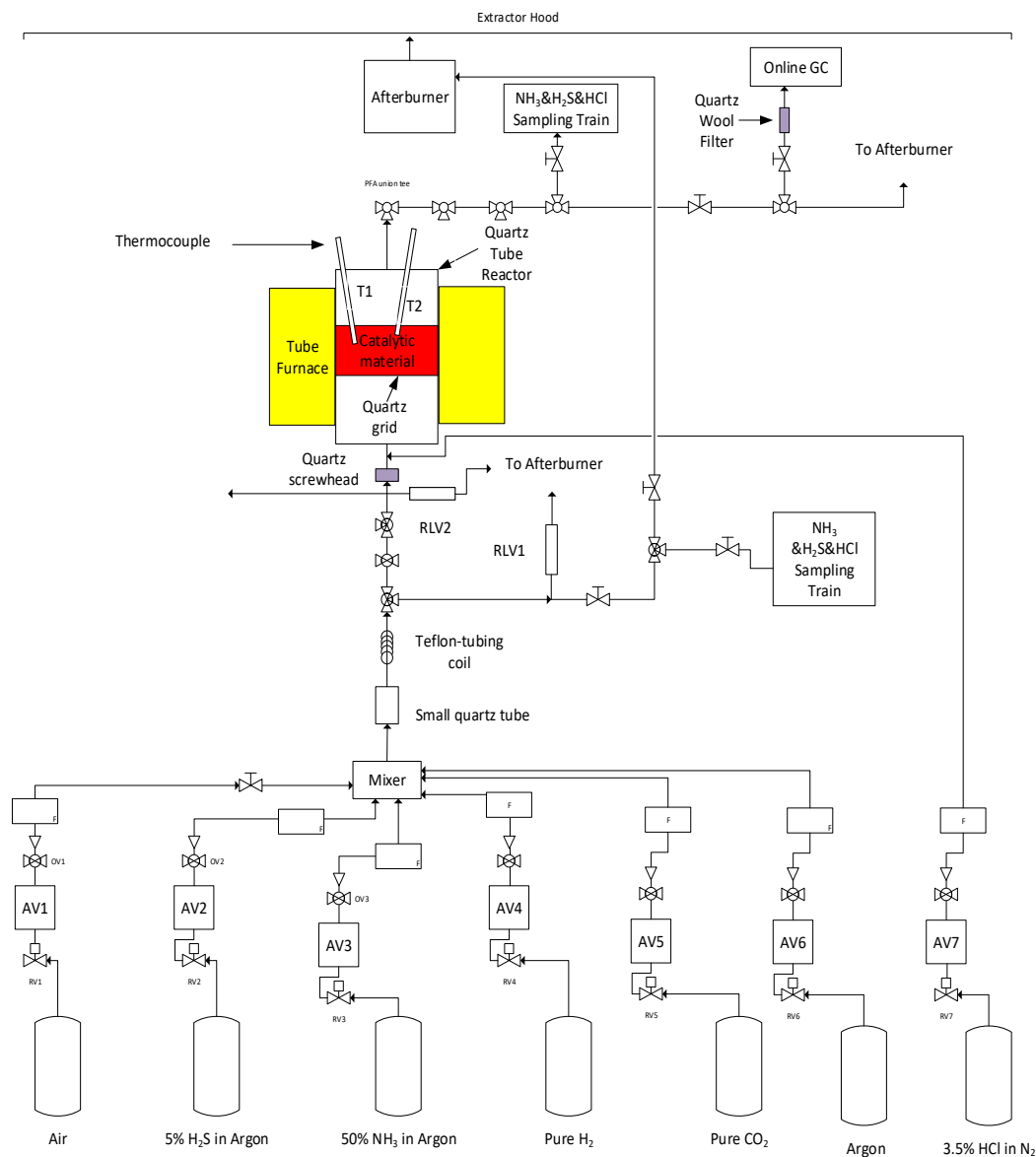
### 2.2. Apparatus and Procedure

This study used a fixed bed reactor system with an inside diameter of 40 mm and length of 815 mm as shown in Figure 1. In each experiment, the reactor tube located inside an electronic furnace was packed with 200 g heat-treated sorbent material (CaO-Fe<sub>2</sub>O<sub>3</sub>) which was kept in place with wool on top. The sorbent material was firstly calcined into CaO at the temperature of 850 °C, and then reduced with H<sub>2</sub> for 40 min at the same temperature. Afterwards, the reactor was cooled to the target carbonation temperature and, once this temperature was reached, the simulated producer gas was injected. The simulated producer gas consists of H<sub>2</sub> (30 vol.%), CO<sub>2</sub> (25 vol%) as well as contaminants of HCl at 200 ppmv, H<sub>2</sub>S at 230 ppmv, and NH<sub>3</sub> at 2300 ppmv with the remaining being Ar as shown in Table 1 which also includes HHV and HHVO values of the feeding gas. Ar was included in the feeding gas instead of N<sub>2</sub> to avoid potential reactions between N<sub>2</sub> and H<sub>2</sub> to form NH<sub>3</sub>.

The target concentrations of these gaseous components were achieved by controlling the flowrates of each gas species using a rotameter or an Alicat mass flowmeter. The carbonation lasted 3 h, and then the feeding gas was changed to air and the temperature was increased again to 850 °C for calcination. After 2 h calcination, the first carbonation/calcination cycle was completed. This process was repeated for the subsequent cycles. For more details of the experimental procedures, see previous publication of [28].

**Table 1.** Composition of simulated gas mixture with their respective O/H, C/H, and HHV values.

Gas Composition (Molar Fraction)	O/H	H/C	HHV (MJ/Nm <sup>3</sup> )	HHVO <sub>2</sub> (kJ/kg O <sub>2</sub> )
CO <sub>2</sub> : 0.25 H <sub>2</sub> : 0.3 Ar: 0.45	0.8	1.2	3.6	14,600



**Figure 1.** Experimental system used in this study [42].

Both in the carbonation and the calcination processes, the overall flowrate of the feeding gas was controlled at 1 SLPM (standard litre per minute) and the outlet gas was analysed by using micro-GC (GC-Agilent 300). Analyses of the contaminants concentrations were carried out using the ion chromatography method (ISE) as discussed in the following section.

### 2.3. Sampling and Analysis of the Contaminants

During calcination and carbonation processes, the contaminant concentrations in the outlet gas streams were measured for the assessment of the contaminant removal and release during the process. The outlet gas stream passed through two parallel bottles which were filled with trapping solutions with a fritted disc to absorb the contaminants in the gas stream. For  $\text{NH}_3$  analysis, 250 mL 0.5 M  $\text{H}_2\text{SO}_4$  was used, whereas for analysis of HCl and  $\text{H}_2\text{S}$ , 250 mL 0.5 M NaOH was used following the procedures described in [43]. The time interval for gas sampling in the carbonation process was 10 min and that in the calcination

process was 20 min, respectively. The calculation of the contaminant removal efficiencies in the carbonation stage was determined using the following equations.

$$\eta_{\text{HCl}} = 1 - \frac{n_{\text{HCl,out}}}{n_{\text{HCl,in}}} = 1 - \frac{V_{\text{HCl,out}}}{V_{\text{HCl,in}}} \quad (3)$$

$$\eta_{\text{NH}_3} = 1 - \frac{n_{\text{NH}_3,\text{out}}}{n_{\text{NH}_3,\text{in}}} = 1 - \frac{V_{\text{NH}_3,\text{out}}}{V_{\text{NH}_3,\text{in}}} \quad (4)$$

$$\eta_{\text{H}_2\text{S}} = 1 - \frac{n_{\text{H}_2\text{S},\text{out}}}{n_{\text{H}_2\text{S},\text{in}}} = 1 - \frac{V_{\text{H}_2\text{S},\text{out}}}{V_{\text{H}_2\text{S},\text{in}}} \quad (5)$$

The volumes of HCl ( $V_{\text{HCl,in}}$ ),  $\text{NH}_3$  ( $V_{\text{NH}_3,\text{in}}$ ) and  $\text{H}_2\text{S}$  ( $V_{\text{H}_2\text{S},\text{in}}$ ) at inlet were calculated based on the gas flow rate and the inlet concentration of the contamination, whereas volumes of contaminants at the outlet ( $V_{\text{HCl,out}}$ ,  $V_{\text{NH}_3,\text{out}}$ ,  $V_{\text{H}_2\text{S},\text{out}}$ ) were based on measured outlet contaminant concentrations and total gas volume.

#### 2.4. Sorbent Characterisation

Characterisation of the sorbent material was performed using  $\text{N}_2$  adsorption analysis to determine the BET surface area and BJH pore volume distribution, scanning electron microscopy (SEM) for microstructure analysis. After the above, analyses were performed again for the used sorbent material.

### 3. Results and Discussion

#### 3.1. $\text{CO}_2$ Capture Efficiency through Carbonation-Calcination Looping

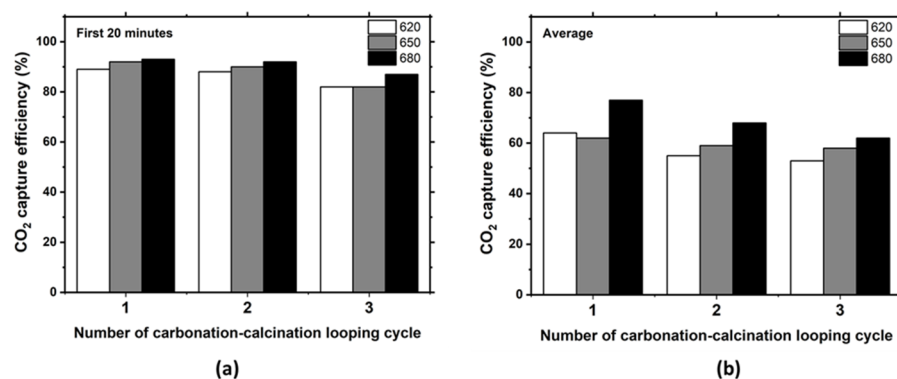
The key objective of this study is to use the  $\text{CaO-Fe}_2\text{O}_3$  based sorbents material to capture  $\text{CO}_2$  from biomass gasification producer gas and release clean  $\text{CO}_2$ -enriched gas stream through a multi-cyclic carbonation-calcination looping. In each run of experiments, the whole carbonation stage lasted for 180 min while the calcination stage was 120 min. However, in practical operation, both carbonation and the calcination stages can be shortened depending on the sorbent activity change with time. Our previous studies have investigated the  $\text{CO}_2$  capture efficiency of the  $\text{CaO-Fe}_2\text{O}_3$  sorbent in the producer gas without contaminants [28] and with contaminants of  $\text{NH}_3$  and  $\text{H}_2\text{S}$  [43] to provide baseline data. In this study, the effect of HCl contaminant was examined in combination with  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , at carbonation temperatures of 620–680 °C to compare with the cyclic  $\text{CO}_2$  capture efficiencies. The following equation was used to calculate the  $\text{CO}_2$  capture efficiency ( $\eta$ ) during carbonation based on the gas volumes over a specified time period at the standard conditions:

$$\eta = 1 - \frac{n_{\text{CO}_2,\text{out}} + n_{\text{CO},\text{out}}}{n_{\text{CO}_2,\text{in}}} = 1 - \frac{V_{\text{CO}_2,\text{out}} + V_{\text{CO},\text{out}}}{V_{\text{CO}_2,\text{in}}} \quad (6)$$

In the above equation,  $V_{\text{CO}_2,\text{in}}$  is the volume of  $\text{CO}_2$  entering the system in the feeding gas mixture (L), and  $V_{\text{CO}_2,\text{out}} + V_{\text{CO},\text{out}}$  are the volume of  $\text{CO}_2$  and  $\text{CO}$  in the outlet (L). In the above equation, part of the inlet  $\text{CO}_2$  is absorbed by the sorbent material, and part of the inlet  $\text{CO}_2$  is transformed into  $\text{CO}$  through the reverse water-gas shift reaction ( $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ). This suggests that higher  $\text{CO}_2$  and  $\text{CO}$  volume in the outlet gas leads to lower  $\text{CO}_2$  capture efficiency of the sorbent material.

Figure 2 shows the average  $\text{CO}_2$  capture efficiencies at three different carbonation temperatures from the feeding gas with contamination of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$ , and HCl. Figure 2a illustrates the results for the first 20 min of carbonation, while Figure 2b shows the results in the entire carbonation process. From Figure 2a,b, it is found that the  $\text{CO}_2$  capture efficiency increased as the carbonation temperature increases, but declined over repeated cycles. At the carbonation temperature of 680 °C, the  $\text{CO}_2$  capture efficiencies throughout the initial 20 min were 93%, 92%, and 87%, respectively, for the first, the second, and the third cycles. Similarly, for the entire carbonation stage at 680 °C, the corresponding  $\text{CO}_2$  capture efficiencies were 77%, 68%, and 62%. In the same way, the effective  $\text{CO}_2$  capture efficiency

at 650 °C in the initial 20 min was 92%, 90%, and 82%, with the corresponding values for the entire carbonation stage being 62%, 59%, and 58%. The CO<sub>2</sub> capture efficiencies in the initial 20 min at carbonation temperature of 620 °C were 89%, 88%, and 81%, and in the entire carbonation stage these were 64%, 55%, and 53%, respectively.

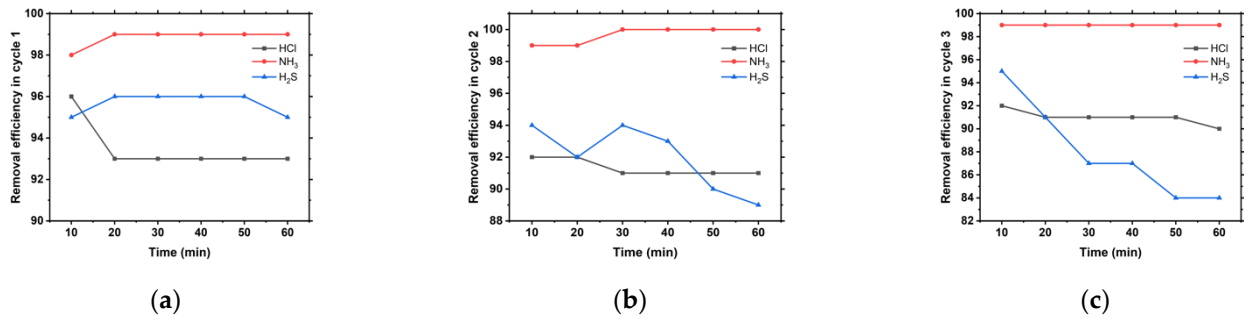


**Figure 2.** CO<sub>2</sub> capture efficiencies of the sorbent material at three carbonation temperatures from the feeding gas with contamination of H<sub>2</sub>S, NH<sub>3</sub>, and HCl: (a) average values in the first 20 min of the carbonation stage, (b) average values through the entire carbonation stage.

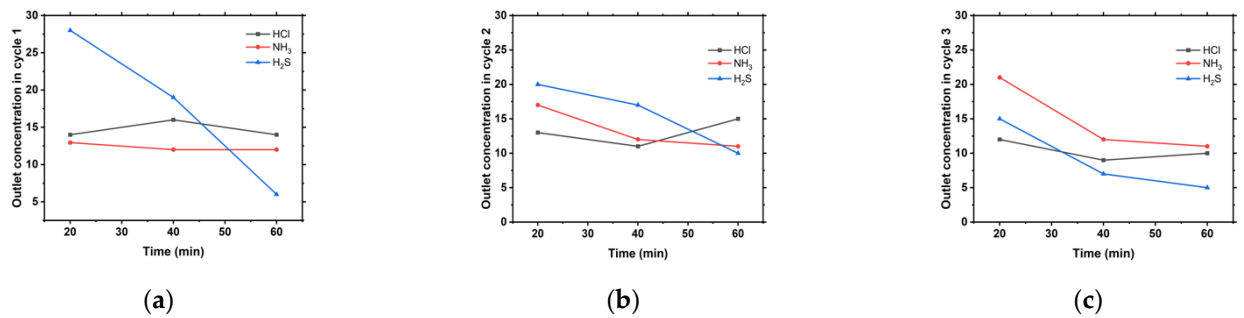
In comparison with previous studies, the CO<sub>2</sub> capture efficiencies of the sorbent material from feeding gas with three contaminants were higher than those with the presence of only NH<sub>3</sub> and H<sub>2</sub>S at the same carbonation temperature. The phenomenon of enhancement of CO<sub>2</sub> capture by HCl can be attributed to chlorination reaction which formed larger-sized pores and decreased the CO<sub>2</sub> diffusional resistance during carbonation, thus, increased sorbent's ability to capture CO<sub>2</sub>. These results were in agreement with other studies with limestone and inert gases. Daoudi et al. [44] conducted thermogravimetric studies and reported that the conversion of CaO was increased from 70% to 90% in the presence of HCl. Studies by Symonds et al. with steam as the feeding gas have also confirmed that adding HCl to the carbonation step results in simultaneous carbonation and chlorination of CaO and their corresponding products are CaCO<sub>3</sub>, CaCl<sub>2</sub>, and CaClOH [24]. These findings support the hypothesis that the formation of chlorination products on the surface of the CaO particles is beneficial. The results in the subsequent Section 3.3 of this paper can be used to further validate this theory through analysis of the chemical and microstructural changes of the sorbent material.

### 3.2. Effect of HCl on Contaminant Removal Efficiencies and Release in the Outlet Gas Stream

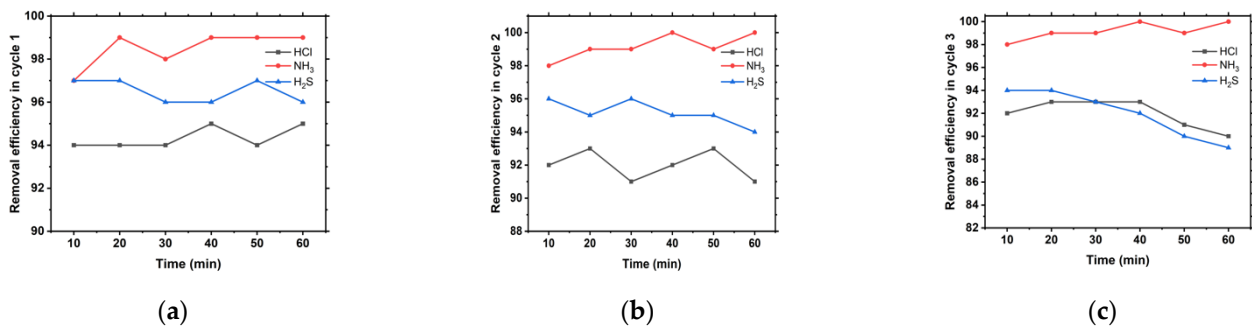
Although the sorbent material was primarily designed to capture CO<sub>2</sub> from a gas stream, it was also capable of decomposing and adsorbing gaseous pollutants. However, it is unknown whether chlorine affects the catalytic and adsorption properties of sorbent material regarding the contaminant removal during the carbonation stage and release during the calcination stage. In this part of study, the contaminant removal efficiency by the CO<sub>2</sub> sorbent material during the carbonation stage and contaminant release during calcination stage were investigated, and the results are shown in Figures 3–6. The results from the first set of experiments suggest that the highest CO<sub>2</sub> capture efficiency was achieved at carbonation temperatures of 650 and 680 °C. Therefore, the contaminant removal efficiencies at these two carbonation temperatures were analysed and presented. Figure 3 shows the contaminant removal efficiencies at different carbonation temperatures of 620, 650, and 680 °C for three cycles. It is anticipated that the CO<sub>2</sub>-rich gas stream from the calcination stage is used in plant nursery greenhouses, thus the contaminant concentrations are important. Figure 4 presents the effect of the carbonation temperature on removal efficiency of combined contaminants (HCl, H<sub>2</sub>S, and NH<sub>3</sub>) during carbonation stage and contaminant concentrations in the outlet gas stream during calcination for the three cycles. In the experiments, the calcination temperature was maintained at 850 °C.



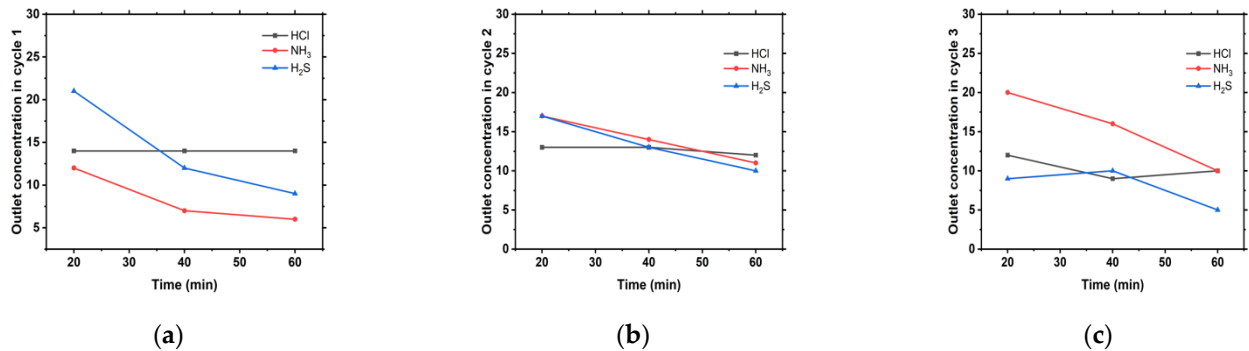
**Figure 3.** The contaminant removal efficiency in the carbonation stage at 650 °C for the first (a), the second (b), and the third cycle (c).



**Figure 4.** The outlet concentrations of contaminants in the calcination stage at carbonation temperature of 650 °C for the first (a), the second (b), and the third cycle (c).



**Figure 5.** The contaminant removal efficiency in the carbonation stage at 680 °C for the first (a), the second (b), and the third cycle (c).



**Figure 6.** The outlet concentrations of contaminants in the calcination stage at carbonation temperature of 680 °C for the first (a), the second (b), and the third cycle (c).

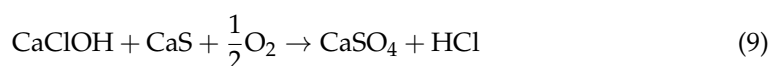
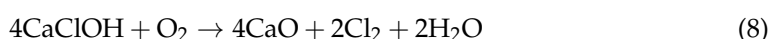
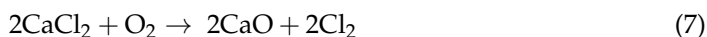
As observed in Figure 3a–c, the HCl removal efficiencies at the carbonation temperature of 650 °C maintained at a relatively high level, above 90%, which did not show a clear change with cycling. Similar results could also be noted for H<sub>2</sub>S removal efficiencies,

95–96% for the first cycle, 89–94% for the second cycle, and 84–95% for the third cycle. These values were higher than those observed in the previous study for combined contaminants of H<sub>2</sub>S and NH<sub>3</sub> [43]. Similarly, the NH<sub>3</sub> removal efficiencies were also improved with values being 98–99% for the first cycle, 99–100% for the second cycle, and 99% for the third cycle. On average over the three cycles, the removal efficiencies 92.1% for HCl, 99.2% for NH<sub>3</sub>, and 91.9% for H<sub>2</sub>S. Correspondingly, the concentrations of the released contaminants in the CO<sub>2</sub>-enriched gas stream were 9–14 ppmv for HCl; 5–28 ppmv for H<sub>2</sub>S and 7–21 ppmv for NH<sub>3</sub> for three cycles of the experiment as shown in Figure 4.

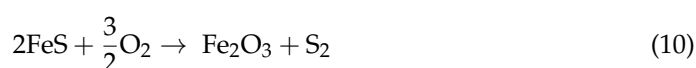
As shown in Figure 5a–c, the contaminant removal efficiencies at carbonation temperature of 680 °C followed the same trend as that at the carbonation temperature of 650 °C. The average removal efficiencies were 92.7% for HCl, 99% for NH<sub>3</sub> was 99%, and 94.7% for H<sub>2</sub>S. These results show that average removal efficiency for HCl was slightly increased and the removal efficiency for H<sub>2</sub>S was increased remarkably with increasing the carbonation temperature due to the increase in gas diffusion into the sorbent material. However, the carbonation temperature had an insignificant impact on the NH<sub>3</sub> removal efficiency. Accordingly, the outlet contaminant concentrations in the CO<sub>2</sub>-enriched gas stream were between 9 and 14 ppmv for HCl; 5–12 ppmv for H<sub>2</sub>S and 6–20 ppmv for NH<sub>3</sub> at the carbonation temperature of 680 °C as shown in Figure 6. The effect of carbonation temperature on the contaminant removal is, in general, consistent with that reported in literature. Lawrence et al. [45] and Wang et al. [30] have reported that the removal efficiencies of the contaminants by calcium-based sorbents increased with the reaction temperature.

Previous research has reported that HCl improves the efficiency of H<sub>2</sub>S removal by calcium-based sorbents [39,46] which is in agreement with the results of this study as shown in Figures 3 and 5. This enhancement has been attributed to the formation of eutectics and pore enlargement [47–49]. In their studies, Matsukata et al. [47], Xie et al. [50], and Zhao et al. [48] suggested that eutectic formation results from the use of the additives (HCl, CaCl<sub>2</sub>), which lead to enhancement of reaction. According to Hu et al. [46] eutectics prevent the pores from becoming closed, thus reducing particle resistance to gas diffusion. In other words, HCl in the feeding gas enhances the reactions between contaminants and unreacted CaO through improved contact. Thus, HCl has a significant positive effect on the sulphur adsorption and ammonia decomposition by sorbent material.

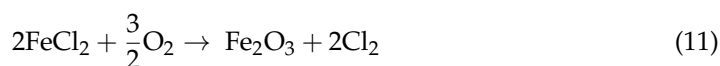
Nevertheless, Figures 4 and 6 show the presence of HCl in carbonation atmosphere has an influence on concentration of released contaminants during calcination. It is worth noting that the level of contaminant concentrations decreased with elapsed time during calcination, although the complete release was not achieved in 60 min. This can be attributed to the sulphidation and release of HCl in the calcination atmosphere as discussed in the following reactions. During carbonation, CaCl<sub>2</sub> from HCl and CaS from H<sub>2</sub>S were formed. After injecting air during calcination, CaCl<sub>2</sub> reacted with O<sub>2</sub> to form Cl<sub>2</sub> as given in reaction (7). Similarly, CaClOH as a chlorination product of CaO also reacted with O<sub>2</sub> in the calcination environment and enhanced Cl<sub>2</sub> release by reaction (8). Further research [51] also confirmed that when the air passed through a sorbent bed in which the sorbents contained CaS and CaClOH, the S-based compounds were released from the sorbent by reaction of (9).



After Fe<sub>2</sub>O<sub>3</sub> in the sorbent material was reduced to Fe, the metal sulphide (FeS) and metal chloride (FeCl<sub>2</sub>) formed in the carbonation stage decompose at higher temperatures in the calcination. This leads to increase in the S-based and the Cl-based species in the outlet gas during the calcination.







From the above discussion, during the experiments with 200 ppmv HCl in the feeding gas in the carbonation, the removal efficiencies of other contaminants were increased, and more S-based and N-based compounds were formed in the sorbent. Accordingly, more S-based and N-based species are released during the calcination, therefore, the contaminant concentrations in the outlet gas stream during the calcination stage are increased.

### 3.3. Microstructure Analysis for Better Understanding of the HCl Effect

In order to better understand the mechanisms of the effect of HCl in the feeding gas on the sorbent performance, the BET surface area, BJH pore volume, and pore size of the fresh and used sorbent material were measured and the results are compared as shown in Table 2. The results from our previous studied with contaminants of NH<sub>3</sub> and H<sub>2</sub>S are also included in the table for comparison.

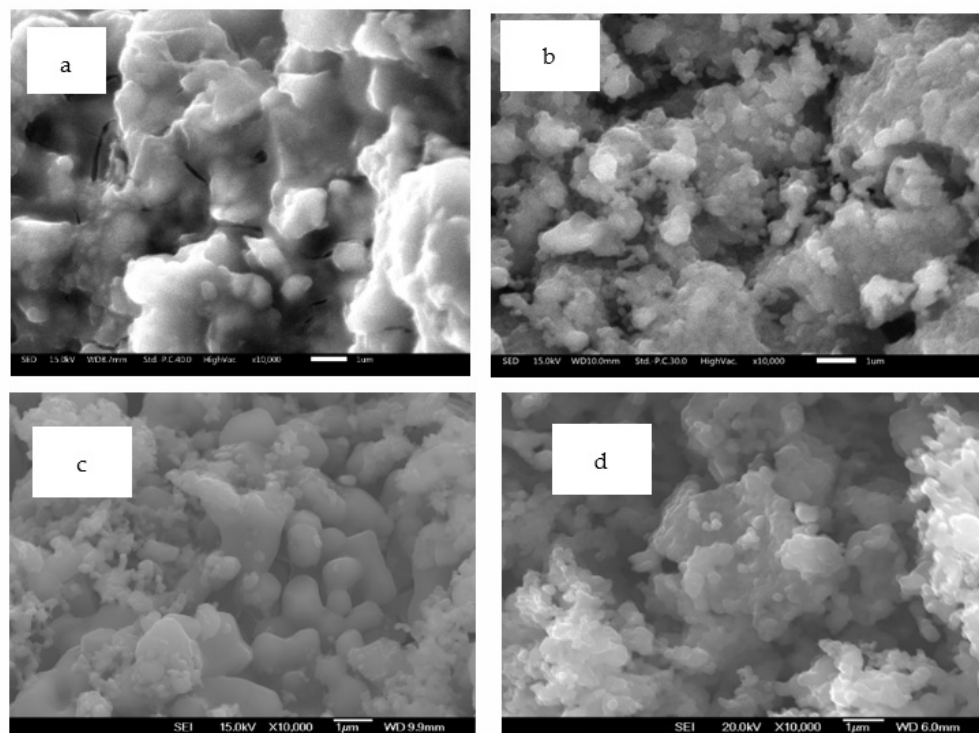
**Table 2.** BET surface area, BJH pore volume, and pore size of the fresh material used sorbent material.

Sample	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Size (nm)
Fresh sorbent material	1.52	0.005	15.50
Used sorbent material with contaminants of NH <sub>3</sub> and H <sub>2</sub> S [43]	1.12	0.001	6.52
Used sorbent material with contaminants of HCl, NH <sub>3</sub> , and H <sub>2</sub> S	1.24	0.001	52.69

From Table 2, it is found that the pore size for the used sorbent material with the presence of HCl in the feeding gas was significantly larger than that of the fresh material and that of used sorbent with contaminants of H<sub>2</sub>S and NH<sub>3</sub>. Based on results of this study, the CO<sub>2</sub> capture efficiency by the sorbent material with presence of HCl in the feeding gas was increased in comparison with that without HCl in the feeding gas. In the former case, the surface of the calcined sorbent was converted to CaCO<sub>3</sub> and, subsequently, reacted with HCl to form CaCl<sub>2</sub>, which reduced the diffusional resistance for the feeding gas to reach the unreacted CaO in the core.

The above findings can be further confirmed by the observation of SEM image which are shown in Figure 7. Figure 7a is the image of the fresh sorbent material, Figure 7b is the image of used sorbent material tested with the feeding gas without any contaminant, Figure 7c is the image of used sorbent material with the feeding gas with contaminants of NH<sub>3</sub> and N<sub>2</sub>S whereas Figure 7d shows the image of used sorbent material tested in the present study. It is observed that the sorbent surfaces with HCl contaminant had more voids that interconnect with each other. This porous structure after chlorination promotes effective solid–gas interaction on the surfaces and thus resulting in higher reactivity. It confirms that the addition of HCl in the feeding gas during the carbonation stage improves the pore structure which is directly related to the improved CO<sub>2</sub> capture and contaminants removal.

From the above observation, the enlarged pore size of the sorbent material with presence of HCl in the feeding gas can be beneficial to CO<sub>2</sub> diffusion through the sorbent particle surface layer and thus to further react with inner CaO. Furthermore, the surface area of the sorbent particle with the presence of combined contaminants (HCl, H<sub>2</sub>S, and NH<sub>3</sub>) in the feeding gas were found slightly larger than those of combined contaminants (H<sub>2</sub>S and NH<sub>3</sub>). This can be the reason why the presence of HCl in the feeding gas improved the CO<sub>2</sub> capture and contaminant removal efficiencies in the three cycles of carbonation–calcination looping. The results from the previous studies also show the formation of CaSO<sub>4</sub> causes pore closure because the molar volume of CaSO<sub>4</sub> is more significant than that of CaCO<sub>3</sub> [42]. However, this result shows that the impact of CaSO<sub>4</sub> on the sorbent material was reduced in the presence of HCl by increasing the surface area and pore size.



**Figure 7.** SEM images of sorbent material with  $\times 10,000$  magnification for: (a) fresh sorbent material, (b) without contaminants, (c) combined  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , (d) combined  $\text{HCl}$ ,  $\text{NH}_3$ , and  $\text{H}_2\text{S}$ .

#### 4. Conclusions

This study investigated the effects of  $\text{HCl}$  presence in the feeding gas during carbonation on performance of a new  $\text{CaO-Fe}_2\text{O}_3$  based sorbent material on simultaneous  $\text{CO}_2$  capture and contaminant removal through carbonation-calcination (CaL) looping. The carbonation temperature of  $680^\circ\text{C}$  is found to be the optimum temperature while the calcination temperature is maintained at  $850^\circ\text{C}$ . The concentrations of contaminants in the exhaust gas during the calcination were also examined which will be used for assessing the applicability of the released  $\text{CO}_2$ -enriched gas stream for target application in plant nursery greenhouses.

This study found that the presence of  $\text{HCl}$  in the feeding gas enhances the removal efficiencies of  $\text{H}_2\text{S}$  and  $\text{NH}_3$  as well as carbonation conversion over repeated CaL looping cycles. The new sorbent material used in the present study is effective in the  $\text{CO}_2$  capture and contaminant removal. At the carbonation temperature of  $680^\circ\text{C}$ , the average efficiencies of contaminant removal were 99%, 94.7%, and 92.7%, respectively, for  $\text{NH}_3$ ,  $\text{H}_2\text{S}$ , and  $\text{HCl}$ . Extending carbonation time results in the drop of  $\text{CO}_2$  capture efficiency, therefore an initial 20 min are favourable for carbonation conversion with efficiency of 93% for the first cycle and 90.6% as average over three looping cycles.

The impact of  $\text{HCl}$  in the feeding gas on the sorbent performance can be related to the formation of large voids on the surfaces of the sorbent particles which reduced the gas diffusion resistance and enhanced the sorbent reactivity. The pore size increase is due to the chlorination process, making the particle surface much more porous.

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