Limestone Decomposition in an O₂/CO₂/Steam Atmosphere Integrated with Coal Combustion

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ABSTRACT: Ca looping is one of the most promising technologies for CO₂ capture. Calcined limestone can be used in the Ca-looping system. It is a low-cost approach to decompose limestone integrated with coal combustion in an O₂/CO₂/steam atmosphere. In this approach, coal combustion heat is continuously supplied for limestone decomposition. We aim to obtain high-purity CO₂ exhaust gas and high-reactivity CaO sorbent. High-purity CO₂ exhaust gas is then further compressed or used. High-reactivity sorbent is then used to capture CO₂ from the coal power plant. However, little research was found to investigate limestone decomposition behavior under oxy-steam combustion conditions. In this study, limestone and coal particles were mixed together and decomposed/combusted in a continuously operating fluidized bed reactor in an O₂/CO₂/steam atmosphere. The results show that increasing O₂ and steam supply reduces the emission of CO, H₂, and SO₂, which enhances the purity of CO₂ exhaust gas. Limestone decomposition conversion is also enhanced with the increase of O₂ and steam supply. Besides, most coal sulfur and ash react with small CaO sorbent particles, which flow out of the reactor and remain in the cyclone. The amount of coal sulfur and ash is very low in a large CaO sorbent particle and has little influence on sorbent reactivity. In situ coal combustion results in a high particle temperature and high limestone decomposition conversion in the fluidized bed but also results in sorbent sintering and a sorbent reactivity decrease. Fortunately, sorbent reactivity is improved by introducing steam into limestone decomposition and a coal combustion atmosphere.

1. INTRODUCTION

The need to reduce the emission of greenhouse gas CO₂ is becoming increasingly important because of global warming. Ca looping is one of the most promising technologies for CO₂ capture in both post-combustion and pre-combustion.¹,² Calcined limestone can be used in the Ca-looping system for CO₂ capture. The basic reactions in the Ca-looping system are carbonation and calcination reactions. CaO sorbent absorbs CO₂ to form CaCO₃, and then CaCO₃ is decomposed to CaO (CO₂ or CO₂/steam atmosphere).³,⁴ However, CaO sorbent reactivity decreases under a high calcination temperature.⁵,⁶

One method to improve CaO sorbent reactivity is steam activation.⁷−⁹ Rong et al.¹⁰ reported that steam hydration of the CaO sorbent after each calcination significantly restrained the rapid decay of CaO sorbent reactivity. Manovic and Anthony¹¹ found that the CaO sorbent after steam reactivation had even better characteristics for CO₂ capture than that of the natural sorbent. In our previous studies,¹² we found that above 1293 K is necessary to decompose limestone near completion in a 100% CO₂ atmosphere, while a high decomposition temperature results in the sorbent reactivity decrease.⁴ Further, we investigated limestone decomposition behaviors in CO₂, CO₂/ N₂, and CO₂/steam atmospheres and found that limestone decomposition conversion and sorbent reactivity could be enhanced in a CO₂/steam atmosphere.³ Then, we also compared coal combustion behaviors in O₂/CO₂ and O₂/ CO₂/steam atmospheres and found that the concentrations of CO, H₂, and CH₄ in the exhaust gas and the contents of sulfur and Al₂O₃ + SiO₂ in the solid product were both lower in an O₂/CO₂/steam atmosphere than an O₂/CO₂ atmosphere.¹²

In conclusion, CaCO₃ should be decomposed in a CO₂/steam atmosphere to obtain high-reactivity CaO sorbent and nearly pure CO₂ exhaust gas. Steam was introduced into the calcination atmosphere to reduce CO₂ partial pressure, which decreased the decomposition temperature of CaCO₃ and increased CaO sorbent reactivity. Besides, sorbent strength is also enhanced by hydration under high steam partial pressure conditions or wet curing core-in-shell pellets with semi-reactive shells.¹⁴

As shown in Figure 1, the Ca-looping process mainly includes two reactors: a carbonation reactor and a calcination reactor. The concept of this Ca-looping process using dual reactors was first proposed by Shimizu et al.¹⁵ The carbonation reaction is an exothermic reaction, and the heat can be recycled for CaCO₃ calcination. In the calcination reactor, the decomposition reaction is an endothermic reaction and a large amount of heat is needed to drive the decomposition reaction. This heat can be supplied from coal combustion because of its low cost and abundance. Moreover, introducing steam into the calcination atmosphere can enhance CaO sorbent reactivity. Therefore, in this study, limestone particles were mixed with coal particles and decomposed/combusted...
together in an O$_2$/CO$_2$/steam atmosphere. Operating like an oxy-fuel circulating fluidized bed combustor can be selected as the calcination reactor. The rapid development for oxy-fuel combustion using a circulating fluidized bed combustor should soon facilitate this calcination option.$^{16,17}$

Many researchers noticed that the heat for the calcination reactor should be supplied through oxy-fuel combustion, but the effect of coal combustion on the limestone decomposition and sorbent reactivity was unclear, especially in an O$_2$/CO$_2$/steam atmosphere. Li et al.$^{18}$ analyzed the process of CO$_2$ capture from flue gas using the carbonation/calcination cycle and considered that a certain amount of coal was burned with pure oxygen in the calcination reactor. However, they just investigated this issue by process simulation but not experimental study about limestone decomposition integrated with coal combustion. Lu et al.$^{19,20}$ considered the heat supply for the calcination reactor using petroleum coke or coal combustion in an atmospheric dual fluidized bed combustion system. They speculated that coal ash and sulfur may influence CaO sorbent reactivity. Later, Lu et al.$^{21}$ also investigated that the sorbent regeneration under realistic calcination conditions contains SO$_2$ in the calcination atmosphere. The results show that sulfate formation blocked active pores/surface area, resulting in lower CO$_2$ capture. Besides, Rodriguez et al.$^{22}$ investigated heat requirements in a calciner, given the mass and heat balances in the system. In addition, calcium-looping process projects have also been industrially demonstrated, including the CaOling project and the Industrial Technology Research Institute (ITRI) project. Experiments were performed in the Institute of Combustion and Power Plant Technology (IFK) 10 kW$_{th}$ facility by Varel et al.$^{23}$ but the calcination reactor was electrically heated. The calcium-looping process project has also been under development at the ITRI of Taiwan in recent years,$^{24,25}$ but the heat for the calciner was from the combustion of liquefied petroleum gas or diesel oil. Most CaOling projects use electrical heating, oxy-fuel biomass combustion, oxy-fuel petroleum coke combustion, or oxy-fuel diesel oil combustion to supply heat for the calcination reactor.

In our opinion, we think that the heat for limestone decomposition could be from the combustion of coal because of its low cost and abundance. Nevertheless, deep experimental research about the effect of coal combustion on the limestone decomposition behavior was rarely found, which was investigated in this study.

It is a good approach to decompose limestone by heat supplied from coal combustion in an O$_2$/CO$_2$/steam atmosphere. We aim to obtain high-purity CO$_2$ exhaust gas and high-reactivity CaO sorbent after limestone decomposition and coal combustion. High-purity CO$_2$ exhaust gas is then compressed and used. High-reactivity CaO sorbent is then used to capture CO$_2$. However, when coal combustion heat is supplied for limestone decomposition in a steam atmosphere, on the one hand, it may result in the emission of CO, H$_2$, NO$_x$, and SO$_2$ gases into CO$_2$ exhaust gas, which influences the purity of CO$_2$ exhaust gas. On the other hand, coal ash and sulfur remain in the CaO sorbent, which may also influence sorbent reactivity. Therefore, in this study, the distributions of the gas phase (CO, H$_2$, NO$_x$, and SO$_2$) and solid phase (coal ash and sulfur) were investigated under various steam and O$_2$ supply conditions in a fluidized bed. Limestone decomposition conversion and CaO sorbent reactivity were also tested. The effects of coal combustion on the limestone decomposition behavior and sorbent reactivity were deeply investigated, especially in an O$_2$/CO$_2$/steam atmosphere. We aim to (1) find a suitable amount of steam and O$_2$ supply for limestone decomposition and coal combustion and (2) clarify the effect of coal combustion on CaO regeneration (limestone decomposition) in this system to obtain high-purity CO$_2$ and high-reactivity CaO sorbent.

2. EXPERIMENTAL SECTION

2.1. Samples. In the present work, Chinese lignite and a kind of limestone were used. They were ground and sieved to 0.25–0.50 mm and mixed together before experiments. The mass ratio of coal/limestone was set at 1:6 (w/w), at which coal was a little excessive to guarantee sufficient combustion heat for the complete decomposition of limestone. Tables 1 and 2 show the properties of the coal sample and chemical composition of the limestone sample, respectively.

Table 1. Properties of the Coal Sample

<table>
<thead>
<tr>
<th>moisture</th>
<th>ash</th>
<th>volatile matter</th>
<th>fixed carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.52</td>
<td>14.60</td>
<td>31.66</td>
<td>41.22</td>
</tr>
</tbody>
</table>

Table 2. Chemical Analysis of Limestone

<table>
<thead>
<tr>
<th>CaO</th>
<th>MgO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>others</th>
</tr>
</thead>
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<tr>
<td>50.57</td>
<td>1.71</td>
<td>3.22</td>
<td>1.05</td>
<td>35.31</td>
</tr>
</tbody>
</table>

2.2. Experimental Procedure. Limestone decomposition and coal combustion were conducted under a continuously operating fluidized bed reactor, as shown in Figure 2. The details of this apparatus were described in our previous work.$^{3,12}$ Temperatures of the fluidized bed reactor and gas preheater were raised to 1223 and 1123 K, respectively. Reactor temperatures were measured through thermocouples located at three different points: T1 (feeding point), T2 (middle of the reactor), and T3 (overflow point). The differential pressure ($\Delta P$) between the bottom and top of the fluidized bed was also measured during experiments.

An O$_2$/CO$_2$/steam stream was introduced into the reactor at a certain flow rate. Experimental conditions were shown in Table 3. At (0.05 L/min) was introduced to prevent the O$_2$/CO$_2$/steam stream from flowing to the overflow holder. Coal and limestone particles were continuously introduced into the fluidized bed reactor to start coal combustion and limestone decomposition. The feeding rate of the mixture was 11 g/min. The decomposed particles were then collected in the overflow holder (large sorbent particle) and cyclone (small...
The decomposition conversion of CaCO₃ to CaO and the carbonation reactivity of the CaO sorbent were both measured through a thermogravimetry (TG) analyzer (TG 209 F3 Tarsus). The decomposition conversion was measured under 1173 K and in a N₂ atmosphere. In the carbonation reactivity test, the temperature was heated to 923 K at a heating rate of 50 K/min in a CO₂ flow of 60 mL/min. Once the temperature reached 923 K, the temperature and the CO₂ flow were stabilized at about 90 min for the carbonation reaction.

3. RESULTS AND DISCUSSION

3.1. Effect of the O₂ Supply on the Gas Distribution. The temperature and ΔP (differential pressure) variations were shown in Figure 3. When the mixture of limestone and coal particle was fed into the reactor at the feeding point, T₁ and ΔP were then increased until the solid particle began to overflow. T₁, T₂, and T₃ reached nearly the same temperature, and ΔP became stable, which indicated that the solid particles were totally fluidized. The time between the start of the particle introduction and the beginning of the overflow was defined as the solid average residence time. The particle residence time varied with the gas flow rate. As shown in Table 3, the particle residence time was about 35 min when the total gas flow rate was about 26 L/min, while it was 60 min when the gas flow rate was about 17 L/min.

The O₂ supply influenced the emission of CO₂, H₂, NO, NO₂, and SO₂, and the results were shown in Figure 4. Excessive emission of CO and H₂ resulted in system energy loss. The O₂ supply was enough for coal combustion before overflowing (35 min), while it was insufficient and CO and H₂ were generated after overflowing (eqs 1–3). Steam participated in combustion and gasification reactions to generate H₂ (eqs 2 and 3). As shown in panels a and b of Figure 4, it was shown that increasing the O₂ supply reduced the emission of CO and H₂, respectively. When the O₂ supply increased from 1.6 to 2.0 L/min, the emission of CO decreased from 7 to 0% and H₂ decreased from 1.3 to 0.05%. The steam gasification reaction (eqs 2 and 3) was inhibited by the increase of the O₂ supply.

\[
\begin{align*}
2C + O_2 &= 2CO \\
C + H_2O &= CO + H_2 \\
CO + H_2O &= CO_2 + H_2 \\
CaCO_3 + SO_2 + 1/2O_2 &= CaSO_4 + CO_2
\end{align*}
\]

Table 3. Experimental Conditions

<table>
<thead>
<tr>
<th>run number</th>
<th>O₂ (L/min)</th>
<th>CO₂ (g/min)</th>
<th>steam (g/min)</th>
<th>particle residence time (min)</th>
<th>temperature T₂ (K)</th>
<th>coal addition</th>
</tr>
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<tr>
<td>1</td>
<td>1.6</td>
<td>12</td>
<td>12</td>
<td>~35</td>
<td>1210</td>
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<tr>
<td>2</td>
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<td>12</td>
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<td>~35</td>
<td>1219</td>
<td>yes</td>
</tr>
<tr>
<td>3</td>
<td>2.0</td>
<td>12</td>
<td>12</td>
<td>~35</td>
<td>1238</td>
<td>yes</td>
</tr>
<tr>
<td>4</td>
<td>1.6</td>
<td>7</td>
<td>8</td>
<td>~60</td>
<td>1213</td>
<td>yes</td>
</tr>
<tr>
<td>5</td>
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<td>7</td>
<td>8</td>
<td>~60</td>
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</tr>
<tr>
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<td>7</td>
<td>8</td>
<td>~60</td>
<td>1240</td>
<td>yes</td>
</tr>
<tr>
<td>7</td>
<td>1.4/2.2</td>
<td>15</td>
<td>0</td>
<td>~60</td>
<td>1165/1190</td>
<td>yes</td>
</tr>
<tr>
<td>8</td>
<td>1.4/2.2</td>
<td>11</td>
<td>4</td>
<td>~60</td>
<td>1173/1198</td>
<td>yes</td>
</tr>
<tr>
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<td>7</td>
<td>8</td>
<td>~60</td>
<td>1184/1208</td>
<td>yes</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
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<td>8</td>
<td>~60</td>
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</tr>
<tr>
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<td>0</td>
<td>17</td>
<td>0</td>
<td>~60</td>
<td>1152</td>
<td>no</td>
</tr>
</tbody>
</table>
Figure 4c showed that NO was increased with the O2 supply, which should be further controlled to obtain high-purity CO2 exhaust gas. The concentration of NO2 was about only 10 ppm in the experiments. In Figure 5a, when the O2 supply increased, the conversion of N to NO increased from 0.70 to 17.09% and N to NO2 increased from 0.02 to 0.45%, respectively. The conversion of N to N2O in an O2/CO2/steam atmosphere was not observed in this study, which has also been proven in a previous study. Therefore, the rest of N in coal was mainly converted to N2. Figure 4d showed that increasing the O2 supply reduced the emission of SO2. The conversion of S to SO2 decreased from 21.56 to 2.46% (Figure 5b). The decrease of SO2 emission was because of the sulfuration reaction (eq 4).

Most SO2 was captured by limestone (CaCO3), especially when O2 was excessive.

3.2. Effect of the Steam Supply on the Gas Distribution. Steam was introduced into the calcination atmosphere to enhance sorbent reactivity. The steam supply also influenced the emission of CO, H2, NO, NO2, and SO2. The emission of CO and H2 was shown in Figure 6. The steam supply was increased from 0 to 4 to 8 L/min (total flow of 15 L/min, with CO2 balance). When the O2 supply was 1.4 L/min, the concentration of CO was about 18, 10, and 17% (dry basis) as the steam supply increased. This concentration was measured on a dry basis, and the actual concentration (wet basis) would be lower than 10 and 17%. CO was converted to CO2 when the steam supply increased (eq 3). It means that the...
emission of CO was inhibited by steam. However, the emission of H2 increased from 0 to 0.7 to 2.8% (dry basis) as the steam supply increased (eqs 2 and 3). The excessive emission of CO and H2 resulted in system energy loss, while an increasing O2 supply can reduce the emission of CO and H2. When the O2 supply was increased to 2.2 L/min, the emission of CO and H2 was nearly zero and exhaust gas was mainly pure CO2.

The emission of NO and SO2 was shown in Figure 7. There was a concentration peak before over-flowing (35 min), which then became stable after over-flowing. The limestone supply was not enough to react with SO2 at the beginning of the experiment; therefore, the emission peak of SO2 (18 min) occurred. When limestone was excessive later, the emission of SO2 decreased and became stable. The stable concentration of SO2 was 60, 60, and 29 ppm (dry basis) as the steam supply increased. Similarly, the actual concentration would be lower than 60 and 29 ppm on a wet basis. The increase of the steam supply accelerated the sulfuration reaction (eq 4)26; therefore, the emission of SO2 decreased. Also, the O2 supply was excessive at the beginning of the experiment; therefore, the emission peak of NO (15 min) occurred. Later, coal was excessive and O2 was not enough for combustion; therefore, the concentration of NO decreased to zero. When the O2 supply increased to 2.2 L/min, the emission of SO2 decreased to zero and the emission of NO increased. The results were similar to panels c and d of Figure 4.

As a summary, when the steam supply was increased to enhance sorbent reactivity, the emission of CO decreased, while H2 increased. Both emissions of CO and H2 were inhibited by the O2 supply increasing, thus minimizing the energy loss in the system. To obtain high-purity CO2 gas, the emission of CO and H2 was reduced to zero through the steam and O2 supplies increasing. However, the emission of NO was increased with the O2 supply increasing, which should be further controlled.

3.3. Limestone Decomposition Conversion under Various Conditions. Most large sorbent particles (mainly containing CaO) were collected in the overflow holder after decomposition, while small particles were collected in the cyclone. The CaO product in the overflow holder could be used to absorb CO2 in flue gas. Limestone decomposition conversion influenced the CO2 absorption efficiency. Limestone was usually decomposed in the CO2 calcination atmosphere, and the decomposition temperature was very high (nearly 1273 K).4 A high decomposition temperature resulted in CaO sorbent sintering and low CO2 absorption efficiency.4,27,28 Therefore, limestone decomposition conversion should be enhanced to improve Ca-looping process efficiency. The decomposition conversion of limestone was measured by TG in this study. The decomposition conversion (X) was defined as follows:

\[
X = \left(1 - \frac{(100 - F_{\text{CO}_2})W_{\text{change}}}{F_{\text{CaO}}(W_0 - W_{\text{change}})} \right) \times 100\%
\]  

where \(F_{\text{CaO}}\) and \(F_{\text{CO}_2}\) are CaO and CO2 contents in limestone (wt %), respectively, and \(W_0\) and \(W_{\text{change}}\) are the initial weight and weight change of the product (g), respectively.

Figure 8a showed the effect of coal addition on limestone decomposition conversion. When only limestone was introduced into the fluidized bed (9 L/min CO2 and 8 L/min steam), the limestone decomposition conversion was 85.12% in the overflow holder, while it was only 57.35% in the cyclone. The decomposition conversion in the cyclone product was lower than that in the overflow holder, which was because small particles easily flowed out and were collected in the cyclone. Therefore, there was not enough time for small particles to be decomposed, which resulted in low decomposition conversion. When coal was mixed with limestone, limestone decomposition conversion was enhanced, especially under oxygen-rich conditions (Figure 8a). In the middle of the fluidized bed reactor, the temperatures (T2) in different conditions were listed in Table 3. The thermocouple was centrally located in the
reactor. This temperature (T2) represented the actual particle temperature. Table 3 shows that the temperature is higher in the coal addition condition than that without coal addition. Coal addition enhances the limestone particle temperature, which results in high limestone decomposition conversion. Moreover, when the O2 supply was increased, the temperature was also increased (Table 3). It means that the limestone particle temperature is higher in oxygen-rich conditions than that in low-oxygen conditions, which also results in a higher limestone decomposition conversion under oxygen-rich conditions (Figure 8a).

Figure 8b showed the effect of the O2 supply and residence time on limestone decomposition conversion. The limestone decomposition conversion increased with the O2 supply because the particle temperature was high in an oxygen-rich atmosphere, as mentioned above. The decomposition conversion was much lower at the residence time of 35 min (1.6, 1.8, and 2.0 L/min O2, 12 L/min CO2, and 12 L/min steam) than 60 min (1.6, 1.8, and 2.0 L/min O2, 9 L/min CO2, and 8 L/min steam). The gas flow rate was much higher at the residence time of 35 min; therefore, the limestone particle was easier to overflow. There was not enough time for limestone decomposition, which resulted in a lower decomposition conversion.

Figure 8c showed the effect of the steam supply on the limestone decomposition conversion. The decomposition conversion of limestone in the overflow holder was higher than that in the cyclone, which has been discussed above. Limestone decomposition conversion was improved by introducing steam into the decomposition atmosphere. When the decomposition atmosphere was diluted by steam, the CO2 partial pressure was then decreased, which resulted in the increase of CaCO3 decomposition conversion.26 Besides, the thermal conductivity of steam is 0.127 W m−1 K−1, which was larger than that of CO2 (0.086 W m−1 K−1). The combustion heat was easily transferred to the limestone particle in a steam dilution atmosphere. Therefore, the limestone particle was easily decomposed in a steam atmosphere.

3.4. Distribution of Coal Sulfur and Ash in the Products. Coal sulfur and ash (mainly containing SiO2 and Al2O3) remained in the sorbent product after coal combustion and limestone decomposition, and they may influence CaO sorbent reactivity. The distributions of coal sulfur and ash in the overflow holder and cyclone under various conditions were shown in Figure 9. Figure 9a showed that the sulfur content in the overflow holder, and cyclone were both increased when the coal particle was mixed to the limestone particle. It was obvious that limestone reacted with SO2 forming CaSO4 (see eq 4). Therefore, the sulfur content in the product was increased. Furthermore, it can also be seen that the sulfur content in the cyclone was much higher than that in the overflow holder, which indicated that SO2 preferred to react with small limestone (or CaO) particles. The size of the limestone particle has great influence on the sulfuration reaction. In the practical application, only large CaO sorbent particles (in the overflow holder) are used to absorb CO2 while small CaO sorbent particles (in the cyclone) are not suitable for CO2 capture because it is easily taken away from the reactor by high-flow-rate gases. The experimental results showed that most sulfur was transferred into small particles, while the sulfur content in the large sorbent particles (in the overflow holder) was very low; therefore, the effect of sulfur on the CaO product reactivity was very weak. Besides, Figure 9a showed that the ash content in the cyclone was also higher than that in the overflow holder. The ash content in the cyclone was increased more obviously than that in the overflow holder when the coal particle was introduced into the reactor. The size of the coal particle was the same as that of the limestone particle (0.25–0.50 mm) before decomposition. However, most volatile matter and fixed carbon in the coal particle was burned off after combustion. Only the small coal ash particle remained in the solid product, and it was easier to flow out. Therefore, most small coal ash was collected in the cyclone. Similarly, the coal ash content in the overflow product was low and had little influence on the CaO sorbent reactivity.

Figure 9b showed the effect of the O2 supply on the distributions of coal sulfur and ash. The sulfur content in the overflow holder and cyclone were both increased as the O2 supply increased. It was mainly because the sulfuration reaction (eq 4) was promoted by the O2 supply increasing. More sulfur was captured by limestone to form CaSO4 under oxygen-rich conditions. However, the O2 supply had little influence on coal ash distribution in Figure 9b. The minor increase of the ash content in the cyclone was mainly due to the little increase of the gas flow rate of O2 (1.6–2.0 L/min), and the small ash particle was easier to flow out under high flow rate conditions.

Figure 9c showed the effect of the steam supply on the distributions of coal sulfur and ash. The steam supply was increased from 0 to 4 to 8 L/min (CO2 balance). The sulfuration reaction (eq 4) was promoted by the steam supply, because the sulfur contents in the overflow product and cyclone product were both increased as the steam supply increased. Manovic et al.30 reported that there were two stages in the sulfuration reaction: an initial faster stage and a diffusion control stage. Steam promoted the initial faster stage reaction because there was greater surface area available for the sulfuration reaction after steam reactivation. They also reported that the presence of steam lowered the activation energy for the
sulfuration reaction. Therefore, the sulfur content in the product was increased through the steam supply. Fortunately, the sulfur content in the large sorbent particle (in the overflow holder) was low; therefore, it had little influence on the sorbent reactivity, even in a steam atmosphere. The ash content in the cyclone product was little increased with the steam supply, while there was a minor decrease in the overflow product. The interaction between Si/Al and limestone was more favored in the O2/CO2 atmosphere than in the O2/CO2/steam atmosphere. The interaction between Si/Al (in small coal ash) and limestone was inhibited by the steam supply; therefore, unreacted Si/Al still remained in the small ash particle and then flowed out.

### 3.5. Reactivity of the CaO Product under Various Conditions

The CaO sorbent reactivity has great influence on CO2 absorption efficiency. In this study, the CaO sorbent was collected in the overflow holder after coal combustion and limestone decomposition. The effect of the steam supply on carbonation reactivity of the CaO product was investigated. As shown in Figure 10, CaO sorbent reactivity was improved when steam was introduced into the decomposition atmosphere. When the steam percentage was increased from 0% (0 L/min) to 25% (4 L/min) to 50% (8 L/min), the final carbonation conversion of CaO sorbent at 120 min was increased from 7.64 to 10.05 to 11.91%, respectively. On the one hand, when the decomposition atmosphere was diluted by steam, the CO2 partial pressure was then decreased. Therefore, limestone was easier to be decomposed, and the decomposition temperature would be lower. Sorbent sintering would not occur under a low decomposition temperature; therefore, the reactivity of the CaO sorbent was improved in a steam dilution atmosphere. This result was also reported by many other researchers. On the other hand, some limestone particles were decomposed to CaO and then hydrated with steam to form Ca(OH)2 in an O2/CO2/steam atmosphere. Ca(OH)2 was not thermodynamically stable at this decomposition temperature. Therefore, Ca(OH)2 existed as a transient species. This Ca(OH)2 was then redecomposed to CaO. The new generated CaO particle was of a higher surface area, which resulted in a higher carbonation reactivity.

As mentioned above, it is a low-cost approach for limestone decomposition integrated with coal combustion. However, coal combustion during limestone decomposition reduced the reactivity of the CaO sorbent by a certain extent, as shown in Figure 11. For example, the final carbonation conversion of the CaO sorbent was about 9.12% in the absence of the coal particle (CO2 atmosphere), while it was only about 7.64% when coal was added to the limestone particle (O2/CO2 atmosphere). Similarly in a CO2/steam atmosphere, the final carbonation conversion of the CaO sorbent was about 10.48% in the absence of the coal particle, while it was about 10.12% (low-oxygen conditions) or even only 8.81% (oxygen-rich conditions) when coal was added to the limestone particle (O2/CO2/steam atmosphere).

First, coal particles and limestone particles were fluidized in the reactor. The limestone particle collided with the high-temperature coal particle, which resulted in not only high limestone decomposition conversion (Figure 8) but also a certain degree of sorbent sintering. The particle temperature was higher under oxygen-rich conditions than low-oxygen conditions (Table 3) because the coal particle was burnt more abundantly under oxygen-rich conditions. A higher local particle temperature resulted in higher sintering, which led to the decrease of sorbent reactivity. Second, SO2 was captured by limestone to form CaSO4 in the outer layer of the sorbent particle. Although this CaSO4 was of little amount in the flow product (Figure 9), it can also cause sorbent particle pore blocking to a certain extent. This blocking was intensified as the O2 supply increased as a result of the sulfuration reaction (eq 4); therefore, the sorbent reactivity was decreased, especially when the sorbent was obtained under oxygen-rich conditions (Figure 8).

Fortunately, the sorbent reactivity was enhanced by introducing steam into the decomposition atmosphere, as shown in Figures 10 and 11. Therefore, we proposed a low-cost approach to decompose limestone integrated with coal combustion in an O2/CO2/steam atmosphere. Coal combustion heat was continuously supplied for limestone decomposition, and steam was introduced into the decomposition atmosphere to enhance sorbent reactivity.

### 4. CONCLUSION

The CaO-based sorbent is usually used to capture CO2 in flue gas from the coal power plant. To obtain high-purity CO2 exhaust gas, CaCO3 (limestone) decomposition must be conducted in a pure CO2 atmosphere. The high-purity CO2 exhaust gas can be compressed or used in practical application. The CaO sorbent is generated from limestone decomposition and then used to capture CO2. However, a lot of heat must be supplied for limestone decomposition. In this study, we proposed that limestone decomposition was integrated with coal combustion to continuously supply heat in an O2/CO2/steam atmosphere.
The results show that the emission of SO₂, CO, and H₂ is not observed when the O₂ supply is enough. High-purity CO₂ exhaust is still obtained after limestone decomposition, even in a coal combustion atmosphere. Besides, limestone decomposition conversion is enhanced because of coal combustion. According to experimental results, most coal sulfur and ash is transferred to small particles (cyclone), while the amount of coal sulfur and ash in the large CaO sorbent particles (overflow holder) is low. In practical application, only the large particles are used to capture CO₂ in the flue gas from coal power plant. Therefore, coal sulfur and ash have little influence on the CaO sorbent reactivity.

This approach has two advantages for CO₂ capture. On the one hand, steam is introduced into the decomposition atmosphere. The results show that limestone decomposition conversion is enhanced and the reactivity of the CaO sorbent is also improved in a steam atmosphere. Besides, the emission of CO and SO₂ is reduced through introducing steam into the decomposition atmosphere, which enhances the purity of CO₂ exhaust gas. On the other hand, limestone (CaCO₃) decomposition is usually decomposed through oxy-fuel combustion. Coal combustion heat is selected for limestone decomposition in this study because of its low cost and abundance. Even the results show that a high coal particle temperature results in a little decrease of sorbent reactivity, but it would also be improved through introducing steam into the decomposition atmosphere.

**REFERENCES**


