**Novel Lime Calcination System for CO₂ Capture and Its Thermal–Mass Balance Analysis**

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**1. INTRODUCTION**

Lime is an important industrial raw material and is widely used in major industries such as iron- and steel-making, flue gas desulfurization, construction, and paper-making industries. Lime is generally obtained by thermal decomposition of limestone into quicklime and carbon dioxide (CO₂) in a shaft kiln or a rotary kiln; thus, lime production is a significant source of carbon emissions. China is currently the largest lime producer in the world with an annual output of more than 200 million tons, accounting for about 70% of the world’s total output. In China, the greenhouse gas emissions caused by lime production increased from 35 million tons of equivalent CO₂ in 1979 to 140 million tons of equivalent CO₂ in 2009; Chinese emissions in 2009 accounted for more than 60% of the world’s emissions related to lime. Thus, there is a pressing need to decrease the emissions of this carbon-intensive sector.

The thermal decomposition reaction equation of limestone is as follows:

\[
\text{CaCO}_3(s) + \text{heat} \rightarrow \text{CaO}(s) + \text{CO}_2(g) \tag{1}
\]

For the conventional calcination process widely used in lime production, as shown in Figure 1a, because of the fuel combustion in the kiln, the above two parts of CO₂ are emitted as flue gas after mixing. Thus, the purity required for CO₂ transportation and storage cannot be achieved because the flue gas contains a large amount of nitrogen, and CO₂ capture requires a gas separation device that consumes a considerable amount of separation energy.

This work proposes a novel lime calcination process with carrier gas heating and air cooling, as shown in Figure 1b. On the one hand, to avoid mixing the CO₂ from limestone decomposition with the flue gas of fuel combustion, the CO₂ used as the circulating carrier gas is employed for heating the limestone. On the other hand, to avoid the carbonation of lime as well as to recover the heat carried by the lime, the air is used for cooling the hot lime. Thus, while obtaining qualified lime products, the tail gas of the new process is expected to be pure CO₂. As a result, the CO₂ from limestone decomposition, which accounts for 70% of the total carbon emission in lime production, can be directly captured without separation of nitrogen and CO₂.
The principle of the reduction in CO₂ emissions of the new process is obvious, but its energy consumption needs to be clarified. In the new process, the partial pressure of CO₂ in the kiln is about five times that of conventional calcination, which means the new process has a greater initial temperature of limestone decomposition. Then, the temperature of the carrier gas discharged from the kiln roof would increase and may increase energy consumption. Therefore, to understand the energy consumption level of the new process and clarify its feasibility, it is necessary to establish the thermal−mass balance model of the new process.

The thermal−mass balance analysis is a common method for calculating energy consumption and thermal efficiency in the industry. There is considerable literature on thermal−mass balance modeling. Among them, some literature works on the shaft lime kiln are as follows.

Zuideveld et al. studied the calculation methods for the design of the preheating zone, reacting zone, and cooling zone of shaft kilns. Zhou et al. established a thermal and material balance model in the lime kiln and performed the thermal process analysis in terms of the main influence factors on the thermal equilibrium state of the lime kiln. Zhou et al. also developed a mathematical model of the reaction and heat-

Figure 1. Comparison of principles: (a) conventional limestone calcination process and (b) new lime calcination process.

Figure 2. Flow scheme of the new lime calcination system.
transfer process in a lime shaft kiln based on the material and energy balance relationship and studied the influence of various operating parameters on the limestone calcination process. Piringer et al. studied the applications of the low calorific value gas in the lime kilns of the iron and steel enterprises. Schwertmann et al. studied the balance calculation of each zone of the lime kiln and obtained heat consumption of the entire kiln through an accurate balance calculation of the reacting zone. Yi et al. established a mathematical model of limestone decomposition and heat transfer based on the principles of thermal and material balance. The influence of operating parameters on the calcination process was then analyzed and optimized. Lang et al. performed a thermal balance analysis of the cooling and heating zones of the shaft kiln and proposed a method to reduce energy consumption. Tong et al. proposed a thermal balance model of the lime kiln and optimized the related process parameters based on the thermal balance analysis. Gutiérrez et al. developed a mass, energy, and exergy balance model to evaluate the performance of a vertical shaft kiln. Rong et al. conducted a comprehensive model analysis to improve the thermal performance of annular shaft kilns with opposite burners.

While the above-mentioned literature is important for energy consumption calculations, operation conditions of the new process are quite different from conventional limestone calcination processes. For instance, the CO₂ pressure of the gas phase in the reacting zone of the new process is about 60 times that of the conventional process. The literature models cannot be applied directly to the new process. Therefore, a thermal—mass balance model for the new process has been developed.

2. PROCESS DESCRIPTION

To facilitate modeling and analysis, the new process was envisioned to a new system from the standpoint of industrial practice in Figure 2, which consists of a new shaft kiln with four processing zones and a furnace system. The shaft kiln is used to convert limestone to lime, and the furnace system is used to provide the heat required for the conversion process. Compared with a conventional one, the new shaft kiln includes a soaking zone. Limestone particles enter the shaft kiln from the kiln roof and slowly drop under gravity. Lime particles are formed and discharged from the bottom of the shaft kiln after preheating, reacting (decomposition), soaking, and cooling. The heat required for the limestone decomposition reaction is carried into the shaft kiln from the furnace system by a circulating carrier gas. Most of the circulating carrier gas enters the reacting zone, and a small part of the circulating carrier gas enters the soaking zone.

In the reacting zone, the rising carrier gas heats the particles, and the limestone in the particles is heated to convert to lime and release CO₂. As a result, the temperature of the carrier gas along its flow direction gradually decreases and the mass flow rate gradually increases. Then, the rising carrier gas continues to enter the preheating zone and heat the limestone particles, but the particle temperature has not reached the limestone’s initial decomposition temperature. Thus, in the preheating zone, the temperature of the carrier gas gradually decreases along its flow direction but the mass flow rate remains unchanged. At the kiln roof, part of the carrier gas is discharged as the tail gas and the rest of the carrier gas is recovered by a high-temperature blower and sent to the furnace system (stove-A in Figure 2) as the circulating carrier gas.

In the soaking zone, the heat conduction occurs in the particles due to the temperature gradient in the particle. The temperature gradient in the particle gradually decreases until the temperature is evenly distributed. The carrier gas flows along the direction of the movement of the particles and exchanges heat with the particles. As a result, the carrier gas temperature gradually decreases to equal to the particle temperature and finally exits the shaft kiln from the bottom of the soaking zone. In the cooling zone, the air cools the particles, and the air temperature gradually increases but its mass flow rate remains unchanged and finally exits the shaft kiln from the top of the cooling zone. The carrier gas discharged from the bottom of the soaking zone and the hot air discharged from the top of the cooling zone are mixed to form an oxidant gas and sent to the furnace system (stove-B in Figure 2), thereby completing the entire cycle.

The new system has several advantages over the conventional process: (1) The CO₂ generated from the limestone decomposition process is used as the carrier gas; thus, a tail gas with high-purity CO₂ can be obtained and captured, while the lime particles are cooled by the air to avoid carbonation. (2) The heat is provided by combustion outside the shaft kiln, and therefore, the flame and the harmful products of the fuel combustion do not contact the particles, which improves the quality of the lime products. (3) By including the soaking zone, the cooling air is prevented from being mixed with the carrier gas in the reacting and cooling zones, thereby ensuring the purity of carrier gas.

3. THERMAL—MASS BALANCE MODEL

The new lime calcination system includes a shaft kiln and a furnace system (as shown in Figure 2). To analyze the thermal—
mass balance of the shaft kiln, Figure 3 shows the temperature distribution schematic curves of each zone in the shaft kiln. Particle processing in the shaft kiln is divided into four zones: preheating, reacting, soaking, and cooling. In the preheating zone, the limestone particles from the kiln roof are preheated to the initial decomposition temperature. In the reacting zone, the limestone is decomposed. In the soaking zone, the heat can homogenize throughout the particle, so that when the particle is discharged from the soaking zone it has a uniform temperature distribution throughout its radius. In the cooling zone, the particles are discharged from the kiln bottom after being cooled. The particle temperature at the junction of the preheating and reacting zones should be equal to the limestone’s initial decomposition temperature. The circulating carrier gas is injected into the kiln at the junction of the reaction and soaking zones, the cooling air is introduced into the bottom of the cooling zone, and the hot air is drawn from the junction of the soaking and cooling zones. Besides, the establishment of the thermal—mass balance model requires the following assumptions: (1) the system is operated under steady-state conditions, (2) the limestone particles only contain CaCO₃, (3) the carrier gas contains only CO₂, (4) heat loss of the shaft kiln and the furnace system is negligible, and (5) the kinetic and potential energies of the gas and solid streams are negligible.

Based on the above conditions, Figure 4 further shows the thermal—mass input and output of the new system. Based on Figure 4, the thermal—mass balance model for the shaft kiln and the furnace system can be established. Especially, the thermal—mass balance of the shaft kiln is discussed in four parts, namely, the preheating, reacting, soaking, and cooling zones.

3.1. Mass Balance Equations of the Shaft Kiln. The mass streams in the shaft kiln include the carrier gas, particle, and air streams. In the preheating, soaking, and cooling zones, the mass flow rate of each stream remains unchanged. In the reacting zone, the limestone decomposes into lime and CO₂ so that the mass flow rate of the particle stream decreases and the mass flow rate of the carrier gas stream increases. The mass balance equation of the carrier gas stream in the reacting zone is

\[ m_g = m_{b} + m_{L}x \]  

(2)

The mass balance equation of the particle stream in the reacting zone is

\[ m_{L}(1 - x) = m_{Q} \]  

(3)

where \( x \) is the CO₂ content in the limestone particle (mass fraction).

3.2. Thermal Balance Equations of the Shaft Kiln. 3.2.1. Preheating Zone. As shown in Figure 4, the heat outputs in the preheating zone include the heat taken away by the carrier gas and the limestone particles and the heat inputs include the heat brought by the carrier gas and the limestone particles. The heat balance equation of the preheating zone is

\[ m_{L} \int_{T_{r}}^{T_{a}} C_{p}^{L} dT = m_{Q} \int_{T_{r}}^{T_{a}} C_{p}^{Q} dT \]  

(4)

where \( m_{L} \) is the mass flow rate of the limestone particles, \( m_{Q} \) is the mass flow rate of the carrier gas, \( T \) is the temperature, \( T_{r} \) is the temperature of the carrier gas entering the preheating zone (leaving the reacting zone), \( T_{a} \) is the environmental temperature, \( T_{r} \) is the tail gas temperature, \( T_{a} \) is the limestone’s initial decomposition temperature, and \( C_{p}^{L} \) and \( C_{p}^{Q} \) are the specific heat capacities of the carrier gas and the limestone particles, respectively. In eq 4, \( T_{r} \) must be greater than \( T_{a} \) and the difference between these two temperatures is the pinch temperature difference of the shaft kiln, that is
\[ \Delta T_{re} = T_r - T_e \] (5)

In practice, the value of \( \Delta T_{re} \) depends on factors such as gas-solid heat-transfer characteristics, particle size, and height of the preheating zone. Therefore, in the model calculation, \( \Delta T_{re} \) is a given parameter in Table 2.

3.2.2. Reacting Zone. As shown in Figure 4, the main heat output in the reacting zone is the decomposition heat of limestone, and the remaining output includes the heat taken away by the carrier gas and the lime particles. The heat inputs include the heat brought by the circulating carrier gas and the limestone particles. The heat balance equation of the reacting zone is

\[
\begin{align*}
& m_h \int_{T_{ref}}^{T_h} C_{p}^{CO_2} \, dT + m_l \int_{T_{ref}}^{T_l} C_{p}^{l} \, dT \\
& = m_Q \Delta h_Q \eta_Q + m_s \int_{T_{ref}}^{T_l} C_{p}^{CO_2} \, dT + m_Q \int_{T_{ref}}^{T_h} C_{p}^{Q} \, dT
\end{align*}
\] (6)

where \( m_h \) is the mass flow rate of the circulating carrier gas entering the reacting zone, \( m_Q \) is the mass flow rate of the lime particles leaving the reacting zone, \( \eta_Q \) is the conversion ratio of limestone, \( \Delta h_Q \) is the reaction enthalpy required for generating a unit mass of lime, \( T_{ref} \) is the reference temperature, \( T_h \) is the temperature of the circulating carrier gas entering the reacting zone (from the furnace system), \( C_{p}^{Q} \) is the specific heat capacity of the lime particles, and \( T_l \) is the average temperature of the lime particles leaving the reacting zone.

The lime particles leaving the reacting zone for the soaking zone have just completed the reaction, and there is a temperature gradient in the particle. Therefore, \( T_l \) in eq 6 is estimated by further assumptions. Indeed, the surface temperature of lime particles can be approximately equal to \( T_{ref} \). By assuming that the lime particles are spherical and the temperature from the surface to the center is linearly distributed (Iliuta et al.23 pointed out that the temperature within the lime particle is slightly different from a linear distribution), then, according to the conservation of energy, \( T_l \) satisfies the following formula

\[
\frac{4}{3} \pi r_0^3 (T_b - T_{ref}) = \int_0^{r_b} 4 \pi r \left( \frac{T_h - T_{ref} + T_l}{r_0} \right) \, dr
\]

where \( r \) is the radial coordinate and \( r_0 \) is the radius of the lime particles. Then, we have

\[
T_b = \frac{3T_b + T_l}{4}
\] (7)

3.2.3. Soaking Zone. As shown in Figure 4, the heat outputs in the soaking zone include the heat taken away by the hot air and the lime particles and the heat inputs include the heat brought by the cooling air and the lime particles. Given that the temperatures of the gas and particles at the bottom of the soaking zone are equal and there is no temperature gradient in the particle, the heat balance equation of the soaking zone is

\[
m_c \int_{T_i}^{T_0} c_{p}^{CO_2} \, dT = m_Q \int_{T_i}^{T_h} C_{p}^{Q} \, dT
\] (8)

where \( T_h \) is the temperature of the carrier gas and the lime particles at the bottom of the soaking zone and \( m_c \) is the mass flow rate of the circulating carrier gas entering the soaking zone.

Under the ideal design condition, no circulating carrier gas should enter the soaking zone (because it will reduce the amount of \( CO_2 \) captured) and no cooling air should be entering the reacting zone through the soaking zone (because it will reduce the \( CO_2 \) purity of the tail gas). However, in actual operation, it is difficult to maintain the above ideal state through pressure balance. As a compromise, a small part of the circulating carrier gas can be lost to ensure the purity of \( CO_2 \) captured, that is, a small part of the circulating carrier gas can enter the soaking zone.

Since the circulating carrier gas entering the reacting zone is finally discharged from the system after passing through the furnace system, \( m_c \) should not be greater than the mass flow rate of the \( CO_2 \) generated in the reacting zone to ensure the mass balance of the system. The larger the \( m_c \), the less the \( CO_2 \) captured through the tail gas recovery. Therefore, the coefficient of lost carrier gas \( \beta \) with a value range of 0–1 is further defined to measure the amount of circulating carrier gas entering the soaking zone, namely, \( \beta = m_c/(m_l - m_Q) \). In practice, the value of \( \beta \) depends on the pressure characteristic of each zone in the shaft kiln. Therefore, in the model calculation, \( \beta \) is a given parameter in Table 2.

3.2.4. Cooling Zone. As shown in Figure 4, the heat outputs of the cooling zone include the heat taken away by the hot air and the lime particles and the heat inputs include the heat brought by the cooling air and the lime particles. The heat balance equation of the cooling zone is

\[
m_Q \int_{T_i}^{T_h} C_{p}^{Q} \, dT = m_a \int_{T_i}^{T_h} C_{p}^{air} \, dT
\] (9)

where \( m_c \) is the mass flow rate of the cooling air, \( T_c \) is the temperature of the hot air, \( T_a \) is the temperature of the lime product discharged from the bottom of the shaft kiln, and \( C_{p}^{air} \) is the specific heat capacity of the air. In eq 9, the lime particle temperature \( T_p \) at the kiln bottom must be higher than the cooling air temperature \( T_c \). The difference between these two temperatures is the bottom temperature difference of the shaft kiln, that is

\[
\Delta T_{pa} = T_p - T_a
\] (10)

In practice, the value of \( \Delta T_{pa} \) depends on factors such as heat-transfer characteristics and the height of the cooling zone. Therefore, in the model calculation, \( \Delta T_{pa} \) is a given parameter in Table 2.

3.3. Decomposition Temperature of Limestone. Solving these thermal–mass balance equations also requires the decomposition temperature of limestone, which is a function of the partial pressure of \( CO_2 \). The formula of limestone decomposition temperature is given as follows24

\[
T_r = \frac{\Delta h_f}{R} \ln \left( \frac{P_0}{P} \right)
\] (11)

where \( \Delta h_f \) is the reaction enthalpy, \( R \) is the gas constant, \( P \) is the partial pressure of \( CO_2 \), and \( P_0 \) is the equation constant. In the new system, the carrier gas is regarded as pure \( CO_2 \), so the partial pressure of \( CO_2 \) is equal to the gas-phase pressure in the kiln.

3.4. Thermal Balance Equations of the Furnace System. The furnace system is equipped with a preheater and two identical regenerative hot stoves (stove-A and stove-B). Stove-A and stove-B are switched for use. When stove-A is in the heat storage step, stove-B is in the heat release step, and vice versa. In the following discussion, stove-A is assumed to be in the
heat release step, and stove-B is in the heat storage step. The fuel of the furnace system is the coal gas, which is common in iron-and steel-making mills, such as the blast furnace gas (BFG) and the Linz–Donawitz gas (LDG), and the combustible component of the coal gas is assumed to be carbon monoxide and completely burned. Then, the thermal balance analysis is performed.

3.4.1. Stove-A. In stove-A, the circulating carrier gas from the shaft kiln roof absorbs the heat released by stove-A to increase its temperature. The heat balance equation of stove-A is

\[ Q_s = \left( m_h + m_i \right) \int_{T_i}^{T_s} C_p^{\text{CO}_2} dT + \int_{T_i}^{T_s} C_p^{\text{air}} dT \]

where \( Q_s \) is the heat-releasing load of stove-A.

3.4.2. Stove-B. In stove-B, the coal gas from the preheater and the oxidant gas from the shaft kiln are mixed and combusted. The high-temperature flue gas stores its heat in stove-B, then flows into the preheater for heat recovery, and finally leaves the system. As shown in Figure 4, the heat outputs of stove-B include the heat taken away by the flue gas and the heat stored. The heat inputs of stove-B include the heat brought by the oxidant gas and the heat and the heat generated by combustion. The heat-storing load of stove-B should be equal to the heat-releasing load of stove-A. The heat balance equation of stove-B is

\[ m_i \int_{T_i}^{T_s} C_p^{\text{CO}_2} dT + m_f \int_{T_f}^{T_s} C_p^{\text{air}} dT + \left( N_i \int_{T_i}^{T_s} C_{p,m} dT + \Delta h_i \right) \]

\[ = Q_s + N_i \int_{T_i}^{T_s} C_{p,m} dT \]

where \( N_i \) is the molar flow rate of the coal gas, \( N_d \) is the molar flow rate of the flue gas, \( \Delta h_i \) is the combustion reaction enthalpy of carbon monoxide (the calorific value of carbon monoxide), \( \gamma_i^{\text{CO}} \) is the molar fraction of carbon monoxide in the coal gas, \( C_{p,m}^{\text{CO}} \) and \( C_{p,m}^{\text{air}} \) are the molar specific heat capacities of the coal gas and the flue gas, respectively, \( T_f \) is the temperature of the coal gas entering stove-B, and \( T_s \) is the temperature of the flue gas discharged from stove-B. Because the stoves are regenerative heat exchangers, \( T_i \) is close to \( T_s \). The difference between these two temperatures is the cold-end temperature difference of the stoves, that is

\[ \Delta T_i = T_s - T_f \]  

In practice, the value of \( \Delta T_i \) depends on the heat-transfer performance of the stoves. Therefore, in the model calculation, \( \Delta T_i \) is a given parameter in Table 2.

In the flue gas, the mole fraction of \( \text{CO}_2 \), the mole fraction of carbon monoxide, and the mole fraction of nitrogen, \( \gamma_i^{\text{CO}_2} \), \( \gamma_i^{\text{CO}} \), and \( \gamma_i^{\text{N}_2} \) are calculated by eqs 15–17, respectively.

\[ \gamma_i^{\text{CO}_2} = \frac{1}{N_i} \left[ N_i + N_f (\gamma_f^{\text{CO}_2} + \gamma_f^{\text{CO}}) \right] \]

where \( N_i \) is the molar flow rate of \( \text{CO}_2 \) in the oxidant gas, \( N_f \) is the molar flow rate of the coal gas, \( \gamma_f^{\text{CO}_2} \) is the mole fraction of \( \text{CO}_2 \), \( \gamma_f^{\text{CO}} \), and \( \gamma_f^{\text{N}_2} \) are the mole fractions of \( \text{CO}_2 \) and carbon monoxide in the coal gas, respectively.

Furthermore, according to Figure 4, the unit energy consumption of the system is composed of four parts, namely, the heat requirement of the limestone decomposition reaction, the waste heat taken away by the tail gas, the waste heat taken away by the flue gas, and the waste heat taken away by the lime product. To examine the proportions of different parts in the unit energy consumption and their changing laws, the
expressions for the different parts in the unit energy consumption are also given below.

The expression of the lime’s decomposition heat is

\[ e_1 = \frac{1}{q_{ce}} \Delta h_{O_2} \eta_{O_2} \]  
(26)

where \( q_{ce} \) is the calorific value of a unit kilogram standard coal.

The expression of the waste heat taken away by the tail gas is

\[ e_2 = \frac{1}{q_{ce}} m_f (\beta - 1) \int_{T_d}^{T_f} rCO_2 \, dT \]  
(27)

The expression of the waste heat taken away by the flue gas is

\[ e_3 = \frac{1}{q_{ce}} m_f \int_{T_d}^{T_f} C_{p,m} \, dT \]  
(28)

The expression of the waste heat taken away by the lime product is

\[ e_4 = \frac{1}{q_{ce}} \int_{T_d}^{T_f} C_p \, dT \]  
(29)

4. RESULTS AND DISCUSSION

A new system with an output of 200 t-d⁻¹ to be used in an iron- and steel-making mill was taken as a case study. First, the system under typical operating conditions is calculated. Second, based on typical working conditions, the following three parameters have been changed to analyze their influence on energy consumption (\( e_1, e_2, e_3, \) and \( e_4 \)), on the flue gas temperatures \( T_d \), on the tail gas temperature \( T_f \), on the flue gas amount \( m_f \) and on the CO₂ captured \( m_r \) (the tail gas amount): the coefficient of excess air \( \alpha \) (Section 4.1), the coefficient of lost carrier gas \( \beta \) (Section 4.2), and the calorific value of coal gas \( q_c \) (Section 4.3). The \( q_c \) is obtained by

\[ q_c = \frac{y_C \Delta h_{CO}}{22.4} \]  
(30)

The \( m_l \) is obtained by

\[ m_l = 86.4 N (y_{CO} M_{CO} + y_{O_2} M_{O_2} + y_{N_2} M_{N_2}) \]  
(31)

where \( M_{N_2} \) is the molecular weight of nitrogen.

The \( m_l \) is obtained by

\[ m_l = 86.4 (m_l - m_{Q} - m_r) \]  
(32)

The \( C_{p,m} \) in eq 13 is calculated by

\[ C_{p,m} = y_{CO} M_{CO} C_{p,CO} + y_{O_2} M_{O_2} C_{p,O_2} + y_{N_2} M_{N_2} C_{p,N_2} \]  
(33)

where \( M_{CO} \) is the molecular weights of carbon monoxide and \( C_{p,CO} \) and \( C_{p,O_2} \) are the specific heat capacities of carbon and monoxide, respectively.

The \( C_{p,m} \) in eq 13 is calculated by

\[ C_{p,m} = y_{CO} M_{CO} C_{p,CO} + y_{O_2} M_{O_2} C_{p,O_2} + y_{N_2} M_{N_2} C_{p,N_2} \]  
(34)

where \( C_{p,CO} \) is the specific heat capacity of oxygen and \( M_{O_2} \) is the molecular weight of oxygen.

The specific heat capacities mentioned above depend on the temperature, which is calculated by the following expression

\[ C_p(T) = C_p^0 \left( \frac{T}{T_0} \right)^n \]  
(35)

where \( C_p^0, T_0, \) and \( n \) are the equation constants. The equation constants for calculating the specific heat capacities of gases and solids used in this work come from the literature²⁵,²⁶ and are listed in Table 1.

In addition to the above specific heat calculation equations (from eqs 33 to 35) and equation constants in Table 1, the main parameters used in this model are listed in Table 2. In Table 2, the 1st to 13th parameters are the operating conditions of the kiln, the 14th to 20th parameters come from the literature,²⁵,²⁶ and the 21st to 23rd parameters are given parameters (namely, the three heat exchange temperature differences, which are set to a reasonable value of 30 °C). In this model, there are 31 unknown variables to be determined by solving 31 equations (from eqs 2 to 32). These variables as well as their calculation results under typical operating conditions are listed in Table 3.

4.1. Influence Analysis of the Coefficient of Excess Air.

The coefficient of excess air is an important operating indicator of fuel combustion. In general, the coefficient of excess air should be as small as possible, but the premise is that the fuel must be completely burned. As shown in Figures 5 and 6, we
analyzed the influence of the coefficient of excess air in the range of 1.0—1.35 on the energy consumption, the flue gas temperature, the tail gas temperature, the flue gas amount, and the CO2 captured (the tail gas amount).

Figure 5 shows that as the coefficient of excess air increases, the waste heat of tail gas $e_2$ and the waste heat of lime product $e_4$ remain unchanged but the waste heat of flue gas $e_1$ increases. Overall, the larger the excess air coefficient, the higher the unit energy consumption. Since the limestone’s decomposition heat $e_1$ is fixed and the waste heat of tail gas $e_2$ remains unchanged, the increase in unit energy consumption is caused by an increase in the waste heat of flue gas $e_1$.

Figure 6 shows that as the coefficient of excess air increases, both the flue gas temperature and the flue gas amount increase, while the tail gas temperature and the CO2 captured (the tail gas amount) keep unchanged. It can be seen that the reason for the increase in the waste heat of flue gas $e_1$ is that the flue gas amount and the flue gas temperature both increase, and the reason that the waste heat of tail gas $e_2$ keeps unchanged is that the tail gas temperature and the tail gas amount both remain unchanged.

In summary, to reduce the unit energy consumption of the system, the coefficient of excess air should be controlled as low as possible.

4.2. Influence Analysis of the Coefficient of Lost Carrier Gas. The lost carrier gas means the circulating carrier gas entering the soaking zone. Allowing a small amount of the circulating carrier gas to enter the soaking zone is a compromise in actual operation. By sacrificing some of the CO2 capture capacity as the expense, the air in the cooling zone will not enter the reacting zone through the soaking zone, which ensures the high purity of the tail gas to facilitate the direct capture of CO2.

As shown in Figures 7 and 8, we analyzed the impact of the coefficient of lost carrier gas in the range of 0—0.35 on energy consumption, the flue gas temperature, the flue gas amount, the tail gas temperature, and the CO2 captured (the tail gas amount).

Figure 7 shows that as the coefficient of lost carrier gas increases, the waste heat of flue gas increases, and the waste heat of tail gas decreases. Since the limestone’s decomposition heat $e_1$ is fixed, and the increase in the waste heat of flue gas $e_1$ offsets the decrease in the waste heat of tail gas $e_2$, the coefficient of lost carrier gas does not significantly influence the unit energy consumption.

Figure 8 shows that as the coefficient of lost carrier gas increases, both the flue gas temperature and the flue gas amount increase, the tail gas temperature remains unchanged, and the CO2 captured (the tail gas amount) decreases. Therefore, the reason for the increase in the waste heat of flue gas $e_1$ is the increase of both the flue gas amount and the flue gas temperature, and the reason for the decrease of the waste heat of tail gas $e_2$ is the decrease in the tail gas amount.

In summary, although the coefficient of lost carrier gas does not influence the unit energy consumption of the system, the increase in the coefficient of lost carrier gas means a decrease in the CO2 captured (the tail gas amount). Therefore, to capture more CO2, the coefficient of lost carrier gas should be controlled as low as possible.

4.3. Influence Analysis of the Calorific Value of Coal Gas. The coal gas, such as BFG or LDG, is a relatively abundant energy source in iron- and steel-making enterprises, whose main combustible component is carbon monoxide. Because different types of coal gas have different carbon monoxide contents, the calorific value of coal gas varies. As shown in Figures 9 and 10, we analyzed the impact of the calorific value of coal gas in the range of 4.5—8.0 MJ·m−3 (from BFG to LDG) on energy consumption, the flue gas temperature, the flue gas amount, the tail gas temperature, and the CO2 captured (the tail gas amount).

Figure 9 shows that as the calorific value of coal gas increases, the waste heat of lime product $e_2$, the waste heat of flue gas $e_1$ and the waste heat of tail gas $e_2$ all have not changed significantly. Since the limestone’s decomposition heat $e_1$ is fixed, the calorific...
value of coal gas does not influence the unit energy consumption of the system.

Figure 10 shows that as the calorific value of coal gas increases, the tail gas temperature and the CO₂ captured (the tail gas amount) remain unchanged, the flue gas temperature increases, and the flue gas amount decreases. The increase of the flue gas temperature offsets the decrease of the flue gas amount, so the waste heat of flue gas $\epsilon_1$ remains unchanged.

In summary, the calorific value of coal gas does not influence the unit energy consumption of the system.

5. CONCLUSIONS

In this work, a lime calcination process with the CO₂ heating and the air cooling was proposed to avoid mixing the CO₂ from limestone decomposition with the flue gas of fuel combustion. This new process was extended to a new system from the
standpoint of industrial practice, which consists of a new shaft kiln and a furnace system. Since the fuel combustion and the limestone decomposition reaction are performed separately, the CO2 from limestone decomposition can be directly captured without separation of nitrogen and CO2. Furthermore, a thermal–mass balance model was developed for the new system, and the energy consumption level of the new system was understood via a case study. The model-based analysis was performed to examine the influence of the key parameters on the performance of the new system. Based on the case study of the new lime calcination system, the main conclusions derived are as follows:

(1) Under typical operation conditions, the unit energy consumption of the new system using BFG as fuel is 142.7 kgce·t−1 and the CO2 captured is 144.8 t·d−1 (the lime output of the system is 200 t·d−1).

(2) The greater the air excess coefficient (ranges from 1.0 to 1.35), the higher the unit energy consumption.

(3) The coefficient of lost carrier gas (ranges from 0 to 0.35) does not influence the unit energy consumption.

(4) The calorific value of coal gas (ranges from 4.5 to 8.0) does not influence the unit energy consumption.

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**NOMENCLATURE**

- \( C_{OP} \) : specific heat capacity of oxygen, kJ·kg−1·K−1
- \( C_{CO} \) : specific heat capacity of carbon monoxide, kJ·kg−1·K−1
- \( C_{CO2} \) : specific heat capacity of the carrier gas (CO2), kJ·kg−1·K−1
- \( \text{MCO} \) : molecular weight of carbon dioxide, kg·mol−1
- \( \text{MCO2} \) : molecular weight of carbon monoxide, kg·mol−1
- \( \text{M2} \) : molar specific heat capacity of the flue gas, kJ·mol−1·K−1
- \( \text{M1} \) : molar specific heat capacity of the coal gas, kJ·mol−1·K−1
- \( \text{M3} \) : specific heat capacity of oxygen, kJ·kg−1·K−1
- \( \epsilon \) : unit energy consumption (kilogram standard coal per ton lime), kgce·t−1
- \( \delta \) : limestone’s decomposition heat, kgce·t−1
- \( \epsilon_{d} \) : waste heat taken away by the lime product, kgce·t−1
- \( \epsilon_{p} \) : waste heat taken away by the flue gas, kgce·t−1
- \( \epsilon_{m} \) : waste heat taken away by the tail gas, kgce·t−1
- \( m_{a} \) : mass flow rate of the air in the cooling zone, t·d−1
- \( m_{b} \) : mass flow rate of the circulating carrier gas entering the reaction zone, t·d−1
- \( m_{c} \) : mass flow rate of the circulating carrier gas entering the preheating zone, t·d−1
- \( m_{d} \) : mass flow rate of the lime particles in the cooling zone, t·d−1
- \( m_{e} \) : mass flow rate of the tail gas (CO2 captured), t·d−1
- \( m_{f} \) : mass flow rate of the circulating carrier gas entering the soaking zone, t·d−1
- \( m_{g} \) : mass flow rate of the tail gas, t·d−1

**ACKNOWLEDGMENTS**

Support from the National Key R&D Program of China (Grant No. 2018YFB0605902) is gratefully acknowledged.

**Notes**

The authors declare no competing financial interest.

**Figure 10.** Influence of the calorific value of coal gas on (a) flue gas temperature and tail gas temperature and (b) flue gas amount and CO2 captured.
$M_{O_2}$: molecular weight of oxygen, kg·mol$^{-1}$

$n$: constant for eq 13

$N_c$: molar flow rate of the circulating carrier gas entering the soaking zone, mol·s$^{-1}$

$N_a$: molar flow rate of the cooling air, mol·s$^{-1}$

$N_d$: molar flow rate of the coal gas, mol·s$^{-1}$

$N_t$: molar flow rate of the flue gas, mol·s$^{-1}$

$p$: gas-phase pressure in the shaft kiln, bar

$q_c$: calorific value of coal gas, MJ·m$^{-3}$

$q_{co}$: calorific value of standard coal, MJ·kg$^{-1}$

$q$: heat-releasing load of stove-A, kW

$r$: radial coordinate, m

$r_0$: radius of the lime particle, m

$R$: ideal gas constant, K

$T$: temperature of the carrier gas leaves the reacting zone, K

$T_c$: temperature of the air leaving the cooling zone, K

$T_d$: temperature of the flue gas discharged from the preheater, K

$T_e$: temperature of the air leaving the cooling zone

$T_h$: temperature of the circulating carrier gas entering the shaft kiln, K

$T_p$: temperature of the lime product, K

$T_s$: temperature of the gas and solid at the bottom of the soaking zone, K

$T_t$: temperature of the carrier gas leaves the reacting zone, K

$T_r$: reference temperature, K

$T_y$: temperature of the flue gas discharged from stove-B, K

$T_{tg}$: temperature of the tail gas, K

$x$: CO$_2$ mass fraction of limestone %

$y_{O_2}$: O$_2$ molar fraction of air, %

$y_{N_2}$: N$_2$ molar fraction of air, %

$y_{CO}$: CO$_2$ molar fraction of the flue gas, %

$y_{O_2}^f$: O$_2$ molar fraction of the flue gas, %

$y_{N_2}^f$: N$_2$ molar fraction of the flue gas, %

$y_{CO}^f$: CO$_2$ molar fraction of the coal gas, %

$y_{C}^f$: CO molar fraction of the coal gas, %

$y_{N_2}^f$: N$_2$ molar fraction of the coal gas, %

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**GREEK LETTERS**

$\Delta h_Q$: reaction enthalpy of generating a unit mass of lime, kJ·kg$^{-1}$

$\Delta h_f^C$: reaction enthalpy of generating a unit mole of lime, kJ·mol$^{-1}$

$\Delta h_f^{CO}$: reaction enthalpy of CO combustion, kJ·mol$^{-1}$

$\Delta T_{pa}$: bottom temperature difference of the shaft kiln, K

$\Delta T_{pe}$: pinch temperature difference of the shaft kiln, K

$\Delta T_{he}$: hot-end temperature difference of the preheater, K

$\Delta T_{ct}$: cold-end temperature difference of the stove, K

$\eta_Q$: conversion ratio of lime, %

$\alpha$: coefficient of excess air

$\beta$: coefficient of the carrier gas

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**ABBREVIATIONS USED**

BFG: blast furnace gas

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