Numerical Simulation of Oxy-Fuel Combustion with Different O₂/CO₂ Fractions in a Large Cement Precalciner

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ABSTRACT: The cement industry is one of the world's largest sources of the anthropogenic CO₂ emissions. Thus, it is very urgent to develop new methods to reduce CO₂ emissions produced by the cement production. In this paper, the oxy-fuel combustion in large-scale cement precalciner was investigated by the large-scale parallel computational fluid dynamics (CFD) numerical simulations. The effects of pulverized coal combustion on the distribution of the velocity field, temperature field, material components, and NO_x concentration were analyzed under O₂/CO₂ molar fractions of 21/79, 25/75, 29/71, 33/67, and 37/63. The results showed that the peak of the temperature is gradually increased, which was beneficial for the decomposition of CaCO₃. The high-purity CO₂ at the outlet can be captured and recycled directly to reduce CO₂ emission. Moreover, the relatively pure CO₂ atmosphere in the furnace significantly reduced the thermal NO_x. The concentration of NO (125–189 mg/m³) during the O₂/CO₂ combustion was much lower than that of conventional air combustion (>800 mg/m³).

1. INTRODUCTION

The greenhouse effect caused by CO₂ emissions is continually increasing, and the challenge of reducing CO₂ emissions is a worldwide problem. The cement industry is one of the world's largest sources of the anthropogenic CO₂ emissions.^{1,2} Therefore, CO₂ emission reduction in the cement industry is an urgent task. The production of cement generates CO₂ emissions in two main ways. It produces CO₂ not only from pulverized coal combustion but also from the decomposition of calcium carbonate.^{1,3} Because the decomposition of CaCO₃ produces the largest share of CO₂ emissions of the process (around 60%) and the combustion of coal represents approximately 40% of the total CO₂ emissions, the CO₂ concentration in the flue gas can reach more than 30%, which is twice the amount produced in a general power station boiler.^{4–6} The methods of reducing CO₂ emissions include the following: CO₂ capture, fuel replacement, heat-transfer efficiency improvement, and clinker consumption reduction. The most promising method is the CO₂ capture technology. CO₂ capture can be further divided into pre-combustion capture, post-combustion capture, and O₂/CO₂ combustion technology.⁶ Among these methods, pre-combustion capture has the lowest efficiency. Post-combustion capture for air combustion is difficult and expensive due to the large amount of N₂ in the flue gas. O₂/CO₂ combustion technology is promising for CO₂ capture due to the pure CO₂ generated by CaCO₃ and thermal NO_x prevention due to the replacement of N₂. Therefore, O₂/CO₂ combustion technology is the most practical method for CO₂ capture in the cement industry.

The cement O₂/CO₂ combustion technology separates the O₂ from the air (because of the high cost of common oxygen production technology, methods for chemical chain oxygen production can also be used⁷) and mixes it with CO₂-rich circulating flue gas, cooling the clinker and generating high-

temperature O₂/CO₂ gas in the cooler (see Figure 1). The high-temperature gas is carried out into the rotary kiln and the precalciner as the secondary or tertiary oxidant for pulverized coal combustion, thereby generating an O₂/CO₂ atmosphere in the kiln and precalciner. The flue gas is relatively pure CO₂ at the outlet, and the gas can be directly captured and recovered. Additionally, the strong radiation ability of polyatomic molecules (e.g., CO₂) will enhance the radiative heat transfer during the clinker calcination, which is beneficial for increasing the strength of the clinker. Furthermore, the CO₂ gas atmosphere prevents the generation of thermal NO_x, thereby greatly reducing the NO_x emission.⁸ Studies have shown that the O₂/CO₂ combustion technology can remove 70–85% of NO in the combustion of solid fuels,^{9,10} and the NO_x emission concentration can be controlled below 100 mg/m³. This is so far lower than the current NO_x emissions national standard (normally 400 mg/m³; 200 mg/m³ in some urban areas) in the existing cement industry.¹¹

Up to now, most researches of O₂/CO₂ combustion are focused on power plants, but less works have been done for cement production. Relatively high CO₂ concentration in calcination will be beneficial for CO₂ capture and recycling and has an advantage for O₂/CO₂ combustion compared with combustion in power plants. Currently, it is costly to demonstrate the O₂/CO₂ combustion technology in actual precalciners and rotary kilns. Although the O₂/CO₂

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Figure 1. Flowchart of oxy-fuel O_2/CO_2 combustion in the cement production.

combustion technology in cement production has been investigated in small trials and theoretical analysis,^{12–14} it is still necessary to promote the development and application of this technology in cement production.

On the other hand, computational fluid dynamics (CFD) technology has become increasingly extensive to the engineering analysis of the cement production with the increasing maturity and precision of CFD.^{15–18} However, most published works are mainly focused on O_2/CO_2 combustion in power station boilers, but only few researches are conducted on cement rotary kilns.^{15–17} Up to now, we have not found the simulating works of O_2/CO_2 combustion in the large-scale cement precalciners except our primary work.¹⁸ Therefore, the 3D numerical simulation is carried out to understand deeply the O_2/CO_2 combustion and decomposition of $CaCO_3$ in large-scale precalciners. Based on the validation of CFD model of O_2/N_2 combustion, the O_2/CO_2 combustion of pulverized coal were simulated under five different O_2/CO_2 fractions in the precaliner for the first time. There will give the effects of O_2/CO_2 combustion on the distribution of flow field and temperature, the burnout ratios of pulverized coal, the decomposition ratios of raw meal, and the NO_x emission in the paper. This will improve practically the application of the O_2/CO_2 combustion technology in cement production.

2. GEOMETRICAL MODEL AND BOUNDARY CONDITIONS

2.1. Geometrical Model. An actual triple-sprayed furnace (TTF) model of the precaliner was selected, which has two shrinkage regions and three spray regions. The dimensions of the precaliner at $Y = 0$ m are shown in Figure 2a. The outer configuration of the precaliner is shown in Figure 2b. The flue gas inlet was located at the bottom, and the outlet was on the top. The precaliner included seven inlets and one outlet. The tertiary wind inlets were located above the lower cone of the furnace and formed a hedging distribution. The pulverized coal burner inlet was arranged 0.5 m above the tertiary wind inlet and was symmetrically distributed at the same height. The

Figure 2. Precaliner structure and mesh.

lower raw meal inlet was located in the first section of the precaliner whose bottom edge was 1.5 m above the pulverized coal inlet. The upper raw meal inlet was located above the first shrinkage region.

The meshes of precaliner were divided into six parts: one lower cone, three body cones, and two shrinkage cones along the Z-axis. Each part was discretized with a structural mesh. Mesh encryption was applied to improve the simulation accuracy near the pulverized coal inlets, the raw meal inlets, the tertiary wind inlets, and the flue gas inlet. The total mesh number was 18.32 million, and the mesh quality was relatively high (with 0.69 of minimum orthogonal quality, 6.63 of maximum aspect ratio). A precisely divided mesh can significantly improve the accuracy of the simulation results, but it will greatly increase the time of computations. The mesh of the precaliner is shown in Figure 2c, and the mesh details of lower part are shown in Figure 2d. The coordinate origin and three points of data validation are marked in it.

2.2. Boundary Conditions. The parameters of the precaliner, the proximate and ultimate analyses of the pulverized coal, and the raw material compositions are

shown in Tables 1–3, respectively. The running capacity of the precalciner was 3800 t/d, and the precalciner accounted for

Table 1. Parameters of the Precalciner

parameters	value
model of precalciner	TTF
production capacity	3800 t/d
coal consumption	11 t/h
height of precalciner	50,000 mm
width of precalciner	5800 mm
gas residence time	5.7 s
average temperature at the outlet	1170 K

60% of the total coal consumption of the cement clinker production line. In the raw material composition, CaO was the main ingredient among the metal oxides. SiO₂ was the main ingredient among the non-metal oxides in the raw meal, and it did not participate in any chemical reaction in the precalciner. Therefore, it was considered to be an inert material and was neglected in the simulations.

The gas phase components of the primary and tertiary winds were set according to O₂/CO₂ volume fractions of 21/79, 25/75, 29/71, 33/67, and 37/63. The parameters of the five conditions are shown in Table 4. Under the five conditions, CO₂ was used to replace all the N₂ in the primary and tertiary winds, as well as inlet flue gas from the rotary kiln. The total gas flow in each condition was varied based on the oxygen concentrations. The same primary wind velocity was used to maintain the stability of the transport of pulverized coal. In order to keep an approximately constant mass flow of the primary wind, the oxygen mass rate in the primary wind was gradually increased for each condition, and the mass flow of the tertiary wind was appropriately lowered to maintain the same amount of total oxygen. At the outlet, a flue gas composition of 1% (vol) O₂ and 99% (vol) CO₂ was set for all five conditions. The boundary condition of the outlet was set as a pressure outlet. The pressure difference between the outlet and the bottom was −200 Pa, based on test data. The excess air coefficient is defined as the ratio of supplied mass flow of oxygen with the theoretical mass flow of oxygen. The excess air coefficient (including the element O in the coal and the O₂ from all the wind inlets and flue gas inlet) was set to 1.1.

2.3. Mesh Independence. It was necessary to verify the mesh independence before the calculation. The total mesh numbers were increased from 18.32 to 21.74 million. The two meshes were used to calculate results separately. The temperature values of three independent points were selected for comparison, and the results are listed in Table 5. The coordinates of the three points were point 1 (0,0,6), point 2 (0,0,10), and point 3 (0,0,14).

As shown in Table 5, the differences of simulated temperature at all three points were maintained within 10 K. Therefore, the simulation with a mesh number of 18.32 million can meet reliably the accuracy requirements to determine the

Table 3. Raw Material Compositions (%)

loss	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO
37.51	13.25	3.09	2.18	41.64	2.33

temperature distribution of the precalciner, and this mesh was selected for the simulation.

3. MATHEMATICAL MODELS AND NUMERICAL METHOD

Commercial CFD software was used to predict the pulverized coal combustion and raw meal decomposition simultaneously in the precalciner and the main results of O₂/N₂ combustion of pulverized coal coincided with the data in the actual precalciner.¹⁸ The models of gas phase, particle phase, and NO_x formation were used, including realizable $k - \epsilon$ model for gas flow and discrete ordinates (DO) model for gas-phase radiation,^{19,20} discrete phase model (DPM) for the particle phase, and PDF model for NO_x formation. The cell-based weighted-sum-of-gray-gas model (WSGGM) was used to calculate gas phase absorption coefficients.^{21,22} These coefficients were refined under oxy-fuel combustion condition due to the strong radiation ability of polyatomic molecules (CO₂).^{23,24}

3.1. Particle Phase Model. The discrete phase model was used to simulate the track of the pulverized coal and the raw meal.^{25,26} The particle scattering factor and emissivity of the coal are set at average constants of 0.6 and 0.9, respectively.²⁰ The discrete random walk model and the stochastic tracking model were used to predict the turbulence in the gaseous phase and the particle dispersion due to the turbulence, respectively (10 size groups of particles are considered, and 31,840 particles are tracked).

The species-transport model was used to express the chemical reactions (including pulverized coal combustion and raw meal decomposition) in the precalciner.^{27,28} Volatile separation and combustion has been assumed to occur first in the coal-combustion process, followed by the combustion of char. The volatile combustion was modeled using the two-competing-rates model. The oxidation reaction of coal is as follows:

The combustion of char was modeled using the particle surface reaction model²¹ in which the first-order Arrhenius model is used. The particle size is assumed to obey the Rosin–Rammler distribution from 10 to 60 μm (mean diameter: 40 μm, spread parameter: 1.54). The oxidation reactions of CO and char are as follows:

Table 2. Proximate and Ultimate Analyses of Coal

proximate analysis (%)					ultimate analysis (%)				Q _{net,ar}
M _{ar}	A _{ar}	V _{ar}	FC _{ar}	C _{ar}	H _{ar}	S _{ar}	N _{ar}	O _{ar}	MJ/kg
9.39	24.79	23.97	41.85	53.97	3.31	0.74	0.84	6.96	20.95

Table 4. Parameters of the Five Conditions

conditions	parameter	gas flue inlet	tertiary wind inlets	primary wind inlets	raw meal inlets	outlet
1	mass flow (kg·s ⁻¹)	28.00	31.32	2.92	54	118.38
2	mass flow (kg·s ⁻¹)	23.51	25.54	2.89	54	108.09
3	mass flow (kg·s ⁻¹)	22.30	21.37	2.85	54	100.66
4	mass flow (kg·s ⁻¹)	17.83	18.21	2.82	54	95.00
5	mass flow (kg·s ⁻¹)	15.88	15.75	2.79	54	90.54
all conditions	temperature (°C)	1020	910	50	780	900

Table 5. Comparison of Temperature Values for Different Mesh Totals

mesh number	point 1 (0,0,6)	point 2 (0,0,10)	point 3 (0,0,14)
18.32 million	1724 K	1505 K	1441 K
21.74 million	1730 K	1497 K	1437 K

The raw meal decomposition is calculated by the particle surface reaction model through the following reaction:

Based on the research of Borgwardt,²⁹ the solving method has been improved to measure the core shrinking process of raw meal.

$$\frac{d(\text{CaCO}_3)}{dt} = -k_s A_{\text{CaCO}_3} \quad (1)$$

where k_s is the rate constant for surface reaction and A_{CaCO_3} is the surface area of calcium carbonate. The kinetic parameters for reactions (R1)–(R5) are summarized in Table 6.

Table 6. Kinetic Parameters of the Reactions

reaction	A	E_a (J/kmol)	reaction orders
R1	2.119×10^{11}	2.027×10^8	$[\text{volatile}]^{0.2}[\text{O}_2]^{1.3}$
R2	2.239×10^{12}	1.7×10^8	$[\text{CO}]^1[\text{O}_2]^{0.25}$
R3	1.04×10^5	9.3×10^7	CO dominant
R4	3.42×10^2	1.3×10^8	CO dominant
R5	5.203×10^8	2.05×10^8	CO ₂ dominant

3.2. NO_x Formation Model. Generally, NO_x are classified as thermal NO_x, fuel NO_x, and prompt NO_x based on different formation paths. Since thermal NO_x is mainly formed above 1500 °C and the internal temperature of a precalciner rarely rises above 1500 °C, thermal NO_x is not likely to be generated in the precalciner, but mainly transmitted from the rotary kiln. Fuel NO_x is formed by nitrogen in the pulverized coal and is the predominant form of NO_x produced in the precalciner. Prompt NO_x only accounts for a small proportion of the total NO_x, so it is negligible. Therefore, the total NO_x has been considered as only fuel NO_x formation.

The probability density function (PDF) model was used to simulate the turbulent interactions in the NO_x formation. For the fuel NO_x, the intermediates of volatile N were considered as 90% HCN and 10% NH₃ for bituminous coal,³⁰ and the intermediate of char N was NO.³¹

3.3. Numerical Methods. The above mathematical models were involved to simulate the effects of oxy-fuel ratios on the combustion process in the precalciner in this paper. The control equations of the fluid phase were discretized by the controlling-volume method, and the equations were solved by a second-order upwind difference scheme. The SIMPLE algorithm was used to couple the pressure and velocity. The

simulating process was finished when the convergence criterion was less than 10⁻⁶ for the continuity, energy, and do-intensity term and less than 10⁻³ for the remaining residuals. In the post-treatment process, the process was repeated until the convergence criterion was less than 10⁻⁸ for the NO_x formation. During the data processing, the burnout ratio of pulverized coal was defined as the ratio of the mass loss of unburned char at the outlet with input coal mass. The decomposition ratio of the raw meal was defined as the ratio of the CaO mass at the outlet with 0.56 times of the CaCO₃ mass.

4. RESULTS AND DISCUSSION

4.1. CFD-Model Validation. Table 7 shows the simulation results at the outlet, which coincide well with those of the field

Table 7. Comparison of Simulation and Field Test^a

parameter	simulation (no air leak)	field test (with air leak)
mass flow at the outlet	197,245 Nm ³ /h	209,648 Nm ³ /h
temperature at the outlet	1174 K	1152 K
O ₂ concentration at the outlet	0.56%	0.79%
CO ₂ concentration at the outlet	27.71%	27.15%
decomposition ratio of raw meal	96.37%	95–98%
NO _x concentration	before SNCR 962 mg/m ³	before SNCR 947 mg/m ³

^aAir combustion with 21% O₂/79% N₂; NO_x concentration, converted into NO₂, based on 10% O₂.

test data (both in air combustion with 21% O₂/79% N₂), showing the consistency and reliability of the simulation. Based on the verified model of the pulverized coal combustion and the decomposition of raw meal, 3D large-scale parallel CFD numerical simulations of O₂/CO₂ combustion were carried out for various oxygen fractions in a Tianhe II-A Supercomputer. The results of the distribution of flow field and temperature, the decomposition ratios of raw meal, and NO_x emission are discussed as follows.

4.2. Distribution of Velocity Field and Temperature.

Due to the volume of O₂ kept as the same for the five operating conditions, when the O₂ fraction gradually increases, the flue gas mass rate is decreased, resulting in a significant decrease in the velocity of flue gas and tertiary wind (shown in Figure 3). The cross-sectional velocity is reduced at the maximum diameter of the precalciner, and the acceleration of the shrinkage becomes weak. Because the actual production rate of clinker is often restricted by the drag force of the flue gas, the clinker production will be greatly enhanced with increasing O₂/CO₂ fractions.

Figure 3. Velocity contours for different O_2 molar fractions in the precalciner: (a)–(e).

As shown in Figure 4, the velocity of the flue gas sharply decreases at the lower cone, and the cross-sectional velocity

Figure 4. Average cross-sectional velocity along the precalciner.

gradually increases and stabilizes at a height of 5 m due to the introduction of tertiary wind. At heights of 16 and 36 m, the two shrinkages significantly accelerate the velocity of the flue gas. The velocity distributions are relatively stable in bodies 2 and 3 of the precalciner. The outlet of the precalciner is located at a height of 50 m, and the negative outlet pressure accelerates the velocity of the flue gas significantly, which is consistent with the results shown in Figure 3. The cross-sectional velocity at the maximum diameter of the precalciner in condition 5 is reduced to 75% of that in condition 1 (treated as the design flow rate), which means that the growth potential of production capacity in condition 5 is about 30% when compared to current production capacity. The partial enlarged view (0–14 m) of velocity distribution in body 1 of the precalciner shown as an inset in Figure 4.

As the oxygen concentration is gradually increased, the maximum temperature in the precalciner gradually increases (see Figure 5). The maximum temperature increases gently when the oxygen concentration is lower than 29%, whereas the maximum temperature increases sharply when the oxygen concentration is greater than 29%. The higher oxygen concentrations accelerate the combustion of coal, resulting in a higher temperature in the precalciner. This is beneficial for the decomposition of $CaCO_3$ but causes higher requirements for the heat resistance of the precalciner material.

The temperature in the precalciner exhibits a decreasing trend upward under all five conditions due to the heat

Figure 5. Temperature contours for different O_2 molar fractions in the precalciner: (a)–(e).

absorption by $CaCO_3$. The distribution of temperature in the precalciner is also affected by the decomposition endotherm of the raw meal. The temperature around raw meal inlets is lower than that of other locations and appears to be V-shaped above both the inlets of the raw meal for the joint effects of velocity and heat absorption by $CaCO_3$. As the oxygen content increases, the maximum temperature increases, and the outlet temperature gradually attenuates.

As shown in Figure 6, the average temperature of the cross-section exhibits the same trend: the higher the oxygen

Figure 6. Average cross-sectional temperature along the precalciner.

concentration, the lower the temperature at the outlet. The heat released by the pulverized coal combustion and the heat absorption of the raw meal are almost the same under the five conditions. A lower amount of flue gas results in less residual heat and a lower temperature at the outlet, which is consistent with the results shown in Figure 5. The partially enlarged view (0–14 m) of temperature distribution in body 1 of the precalciner is shown as an inset in Figure 6. As shown in Figure 7, the maximum temperatures of the cross section at $Z = 6$ m exhibits a trend of increasing gradually, while the average temperatures of the cross section at $Y = 0$ m exhibits a trend of decreasing gradually, which is also consistent with the results shown in Figure 5.

4.3. Distribution of CO_2 , CaO , and $CaCO_3$. As shown in Figure 8, with increasing oxygen fraction for five conditions, the flow rate of flue gas decreases and so does the primary and tertiary wind, resulting in the gradual attenuation in the flow zone above the tertiary wind inlets. When the two raw meals enter, it leads to a local decrease in the CO_2 mass fraction (the

Figure 7. Maximum and average temperatures for different O_2 molar fractions.

Figure 8. CO_2 mass fraction contours for different O_2 molar fractions in the precalciner: (a)–(e).

mass share of CO_2 in total gas–solid flow). After which, a large amount of CO_2 is generated by the decomposition of raw meal, and CO_2 then increases. The decomposition ratio is on the same level from the highest value of 94.22% at condition 1 to the lowest value of 92.02% at condition 5, indicating that the high concentration of the CO_2 atmosphere has no effect on the production. As shown in Figure 9, the tertiary wind has a strong dilution effect on the CO_2 concentration at a height of 5 m, whereas the two raw material inlets at heights of 9 and 19 m have large influences on the CO_2 concentration, which is consistent with the conclusion of Figure 8. The partially

Figure 9. Average cross-sectional CO_2 mass fraction along the precalciner.

enlarged view (0–14 m) of CO_2 concentration in body 1 of the precalciner is shown as an inset in Figure 9.

The gas-phase composition is calculated after gas–solid separation, as shown in Table 8. As the amount of flue gas decreases, the ratios of O_2 and H_2O increases slightly, while the ratio of CO_2 decreases correspondingly. However, the concentrations of each component are similar in all five conditions. High-purity CO_2 is obtained from the outlet in all five conditions, which is convenient for direct capture and recycling.

As shown in Figure 10, CaO mass fraction (the mass share of CaO in total gas–solid flow) reaches a higher level earlier due to the decrease of flue gas and tertiary wind. The CaO mass fraction reaches a level of 24–27% at heights of 47 m for condition 1, 23 m for condition 2, and 11–13 m for conditions 3–5. Above the main combustion zone, heat released by the pulverized coal combustion is basically completed at a residence time of 1.5 s due to the exhaust of O_2 , while the decomposition of $CaCO_3$ is also basically completed within the same residence time. Therefore, the effects caused by the decrease of velocity on coal combustion and $CaCO_3$ decomposition are relatively limited. The mass flow rates of CaO are similar at the outlet in all five conditions, which means that the decomposition ratio of the raw meal is on the same level. As shown in Figure 11, the CaO formation rate is extremely high in the range of 6–16 m, indicating that the decomposition ratio of the raw meal is higher in the higher-temperature region, and the enrichment of the raw meal is flatter above 20 m, which is consistent with the results of Figure 10. The decomposition ratios of the raw meal in all five conditions are similar at the outlet. The partially enlarged view (0–14 m) of CaO distribution in body 1 of the precalciner is shown as an inset in Figure 11.

As shown in Figure 12, $CaCO_3$ mass fraction (the mass share of $CaCO_3$ in total gas–solid flow) distributions are similar for all five conditions. In the region around the two raw meal inlets, the mass fraction of $CaCO_3$ is high and decays very rapidly upward due to the partially high temperature caused by the pulverized coal combustion, indicating that the decomposition ratio is relatively high in this region (within a residence time of 1–1.5 s). The minimum mass fraction of the raw meal occurs at the outlet, and the decomposition ratio of the raw meal is similar for all five conditions, indicating that the high concentration of the CO_2 atmosphere has no effect on the production. As shown in Figure 13, the mass fraction of $CaCO_3$ reaches local peaks at heights of 9 and 20 m separately around the raw meal inlets. Furthermore, the decomposition ratio of $CaCO_3$ at the lower inlet is significantly higher than that at the upper inlet, which is in coincidence with temperature distribution. The partially enlarged view (0–14 m) of $CaCO_3$ distribution in body 1 of the precalciner is shown as an inset in Figure 13.

4.4. Distribution of O_2 and NO. As shown in Figure 14, the O_2 in the precalciner is mainly provided by the primary and tertiary winds, thus, the highest concentration of O_2 appears near the inlets of the primary and tertiary winds. The higher oxygen concentration in the main combustion zone accelerates the reaction rate due to the increased number of effective collisions, resulting in a higher temperature in the precalciner, which is in coincidence with the temperature distribution in Figure 5. The oxygen concentration ranges from 0.67 to 1.35 vol % and is approximately at the same level at the outlet in all five conditions (a lower amount of flue gas corresponded to a

Table 8. Comparison of Flue Gas Composition (Mole Fraction) At the Outlet

parameter	condition 1	condition 2	condition 3	condition 4	condition 5
O ₂	0.67%	0.77%	0.92%	1.10%	1.35%
CO ₂	94.64%	93.94%	93.23%	92.53%	91.81%
H ₂ O	4.69%	5.30%	5.85%	6.37%	6.84%

Figure 10. CaO mass fraction contours for different O₂ molar fractions in the precalciner: (a)–(e).

Figure 11. Average cross-sectional CaO mass fractions along the precalciner.

Figure 12. CaCO₃ mass fraction contours for different O₂ molar fractions in the precalciner: (a)–(e).

higher concentration of remaining O₂). Trace oxygen concentration at the outlet proves the full burnout of pulverized coal and is in coincidence with the excess air coefficient 1.1. The O₂ concentration is less than 1 vol % in the

Figure 13. Average cross-sectional CaCO₃ mass fractions along the precalciner. Figure 14. Contours of different O₂ molar fractions in the precalciner: (a)–(e).

rest of the precalciner for the same reason. The partially enlarged view (0–14 m) of O₂ concentration in body 1 of the precalciner is shown as an inset in Figure 15.

To study the NO formation in the precalciner in a more isolated manner, the mass flow rate of NO is fixed in the flue

Figure 15. Average cross-sectional O₂ mass fractions along the precalciner.

gas. As the amount of flue gas decreases in the five conditions, the concentration of NO gradually increases. Since the O₂/CO₂ atmosphere completely prevents the generation of thermal NO_x, the precalciner only contains a small amount of fuel NO_x generated by the pulverized coal combustion, and NO_x is transferred into the precalciner by the flue gas. As shown in Figure 16, the NO_x concentration stabilizes at the

Figure 16. NO concentration contours for different O₂ molar fractions in the precalciner: (a)–(e).

first shrinkage due to the dilution of the ascending gas in all five conditions. The NO_x concentration ranges from 116 to 181 ppm (the NO₂ concentration ranges from 125 to 189 mg/m³ according to the national standard) at the outlet. The NO₂ concentration at the outlet is much lower than 900 ppm, which is the approximate concentration in the conventional O₂/N₂ process. As shown in Figure 17, a local peak of the NO

Figure 17. Average cross-sectional NO concentration along the precalciner.

concentration occurs at a height of 6 m due to the fuel NO_x released by the pulverized coal combustion, after which the NO concentration gradually decays and tends to be stable in the upward direction, which is consistent with the conclusion of Figure 16. The NO_x concentrations of the cross section at Z = 6 m are shown in Figure 18. The NO concentration reaches a higher concentration value at this point as the amount of flue gas decreases, which is consistent with the conclusion of Figure 17. The partially enlarged view (0–14 m) of NO_x concentration in body 1 of the precalciner is shown as an inset in Figure 17. As shown in Figure 19, the NO concentrations in the three conditions with O₂ concentrations

Figure 18. NO fraction contours for different O₂ molar fractions at Z = 6 m: (a)–(e).

Figure 19. NO₂ concentration at the outlet with different O₂ molar fractions.

above 29% are significantly lower than those of the two conditions with O₂ concentration below 25%, which indicates that when oxy-fuel combustion is used, the O₂ concentration recommended is ≥30%.

5. CONCLUSIONS

An actual TTF precalciner of O₂/CO₂ combustion was simulated using 3D large-scale parallel CFD numerical simulations with a validated model. The results of simulation for five various O₂/CO₂ fractions were concluded as follows:

- (1) As the concentration of O₂ increases, the peak of the temperature gradually increased, which could enhance the decomposition of CaCO₃ but created higher requirements for the heat resistance of the precalciner material.
- (2) The O₂/CO₂ combustion technology can enhance the production capacity of precalciner and the high-purity CO₂ at the outlet can be directly captured and recycled.
- (3) The relatively pure CO₂ atmosphere in the furnace greatly reduced NO_x formation. The concentration of NO at the outlet (125–189 mg/m³) was much lower than that of conventional air combustion (>800 mg/m³), which is beneficial for reducing the operating costs of ammonia injection.

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Notes

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REFERENCES

- (1) Gao, T.; Shen, L.; Shen, M.; Liu, L.; Chen, F.; Gao, L. Evolution and projection of CO₂ emissions for China's cement industry from 1980 to 2020. *Renewable Sustainable Energy Rev.* **2017**, *74*, 522–537.
- (2) IEAGHG. Deployment of CCS in the cement industry: 2013/19. http://www.ieaghg.org/docs/General_Docs/Reports/2013-19.pdf (accessed 16.02.20), 2013.
- (3) Huntzinger, D. N.; Eatmon, T. D. A life-cycle assessment of Portland cement manufacturing: comparing the traditional process with alternative technologies. *J. Clean. Prod.* **2009**, *17*, 668–675.
- (4) Gang, L.; Lu, J. D.; Liu, Z. X.; Xue, J. T.; Xie, X. H.; Zeng, K.; Hu, Z. J. NO reduction by coal and char at different CO₂ concentrations in cement precalciner (in Chinese). *J. Combust. Sci. Technol.* **2012**, *1*, 50.
- (5) Scheffknecht, G.; Al-Makhadmeh, L.; Schnell, U.; Maier, J. Oxy-fuel coal combustion – A review of the current state-of-the-art. *Int. J. Greenhouse Gas Control* **2011**, *5*, S16–S35.
- (6) Carrasco-Maldonado, F.; Spörl, R.; Fleiger, K.; Hoenig, V.; Maier, J.; Scheffknecht, G. Oxy-fuel combustion technology for cement production – State of the art research and technology development. *Int. J. Greenhouse Gas Control* **2016**, *45*, 189–199.
- (7) de Lena, E.; Spinelli, M.; Gatti, M.; Scaccabarozzi, R.; Campanari, S.; Consonni, S.; Cinti, G.; Romano, M. C. Techno-economic analysis of calcium looping processes for low CO₂ emission cement plants. *Int. J. Greenhouse Gas Control* **2019**, *82*, 244–260.
- (8) Liu, H.; Zailani, R.; Gibbs, B. M. Pulverized coal combustion in air and in O₂/CO₂ mixtures with NO_x recycle. *Fuel* **2005**, *84*, 2109–2115.
- (9) Toftegaard, M. B.; Brix, J.; Jensen, P. A.; Glarborg, P.; Jensen, A. D. Oxy-fuel combustion of solid fuels. *Prog. Energy Combust. Sci.* **2010**, *36*, 581–625.
- (10) Zou, C.; Huang, Z. J.; Chu, K.; Gui, X. L.; Qiu, J. H.; Zhang, L. Q.; Zheng, C. G. A pilot scale study on SO₂ and NO_x emission control in O₂/CO₂ recycled coal combustion (in Chinese). *Proc. CSEE* **2009**, *29*, 20–24.
- (11) State Environmental Protection Administration, General Administration of Quality Supervision, Inspection and Quarantine. Emission standard for air pollutants in cement industry (GB 4915-2013). Beijing: China Environment Press.
- (12) Telesca, A.; Marroccoli, M.; Tomasulo, M.; Valenti, G. L.; Dieter, H.; Montagnaro, F. Low-CO₂ cements from fluidized bed process wastes and other industrial by-products. *Combust. Sci. Technol.* **2016**, *188*, 492–503.
- (13) Paneru, M.; Mack, A.; Hornberger, M.; Cinti, G.; Ruppert, J.; Maier, J. Impact of oxyfuel technology on calcination process. *GHGT-14 Melbourne*; **2018**.
- (14) Granados, D. A.; Chejne, F.; Mejía, J. M. Oxy-fuel combustion as an alternative for increasing lime production in rotary kilns. *Appl. Energy* **2015**, *158*, 107–117.
- (15) Granados, D. A.; Chejne, F.; Mejía, J. M.; Gómez, C. A.; Berrio, A.; Jurado, W. J. Effect of flue gas recirculation during oxy-fuel combustion in a rotary cement kiln. *Energy* **2014**, *64*, 615–625.
- (16) Wang, M.; Liao, B.; Liu, Y.; Wang, S.; Qing, S.; Zhang, A. Numerical simulation of oxy-coal combustion in a rotary cement kiln. *Appl. Therm. Eng.* **2016**, *103*, 491–500.
- (17) Ditaranto, M.; Bakken, J. Study of a full scale oxy-fuel cement rotary kiln. *Int. J. Greenhouse Gas Control* **2019**, *83*, 166–175.
- (18) Zhang, L.; Wei, X.; Li, S.; Zhai, Y. Numerical simulation of O₂/CO₂ combustion in large cement precalciner (in Chinese). *Sci. Sin. Technol.* **2019**, *49*, 1080–1088.
- (19) Shih, T. H.; Liou, W. W.; Shabbir, A.; Yang, Z.; Zhu, J. A new k-ε eddy-viscosity model for high reynolds number turbulent flows-model development and validation. *Comput. Fluids* **1995**, *24*, 227–238.
- (20) Yin, C. On gas and particle radiation in pulverized fuel combustion furnaces. *Appl. Energy* **2015**, *157*, 554–561.
- (21) Álvarez, L.; Yin, C.; Riaz, J.; Pevida, C.; Pis, J. J.; Rubiera, F. Oxy-coal combustion in an entrained flow reactor: application of specific char and volatile combustion and radiation models for oxy-firing conditions. *Energy* **2013**, *62*, 255–268.
- (22) Yin, C.; Rosendahl, L. A.; Kær, S. K. Chemistry and radiation in oxy-fuel combustion: a computational fluid dynamics modeling study. *Fuel* **2011**, *90*, 2519–2529.
- (23) Guo, J.; Liu, Z.; Huang, X.; Zhang, T.; Luo, W.; Hu, F.; Li, P.; Zheng, C. Experimental and numerical investigations on oxy-coal combustion in a 35 MW large pilot boiler. *Fuel* **2017**, *187*, 315–327.
- (24) Guo, J.; Liu, Z.; Wang, P.; Huang, X.; Li, J.; Xu, P.; Zheng, C. Numerical investigation on oxy-combustion characteristics of a 200MWe tangentially fired boiler. *Fuel* **2015**, *140*, 660–668.
- (25) Rahmanian, B.; Safaei, M. R.; Kazi, S. N.; Ahmadi, G.; Oztop, H. F.; Vafai, K. Investigation of pollutant reduction by simulation of turbulent non-premixed pulverized coal combustion. *Appl. Therm. Eng.* **2014**, *73*, 1222–1235.
- (26) Gómez, M. A.; Porteiro, J.; de la Cuesta, D.; Patiño, D.; Míguez, J. L. Numerical simulation of the combustion process of a pellet-drop-feed boiler. *Fuel* **2016**, *184*, 987–999.
- (27) Musto, M.; Rotondo, G. CFD analysis of a realistic reduced-scale modeling equipped with axial jet fan. *Fire. Saf. J* **2015**, *74*, 11–24.
- (28) Branco, J.; Coelho, P. J.; Costa, M. Experimental and numerical investigation of turbulent diffusion flames in a laboratory combustor with a slot burner. *Fuel* **2016**, *175*, 182–190.
- (29) Borgwardt, R. H. Calcination Kinetics and Surface Area of Dispersed Limestone Particles. *AIChE J.* **1985**, *31*, 103–111.
- (30) Winter, F.; Wartha, C.; Löffler, G.; Hofbauer, H. The NO and N₂O formation mechanism during devolatilization and char combustion under fluidized bed conditions. *Symp. (Int.). Combust.* **1996**, *26*, 3325–3334.
- (31) Lockwood, F. C.; Romo-Millanes, C. A. Mathematical modelling of fuel-NO emissions from PF burners. *J. Int. Energy* **1992**, *65*, 144–152.