MODELING OF Cu OXIDATION IN ADIABATIC FIXED-BED REACTOR WITH N₂ RECYCLING IN A Ca/Cu CHEMICAL LOOP

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Abstract

A dynamic model has been constructed to describe the Cu oxidation reaction within a large-scale Cu/CuO chemical looping process in adiabatic fixed-bed reactors. Careful control of the temperature is required during Cu oxidation because of its high reaction enthalpy. The recycling of a large amount of nitrogen, previously cooled down, and its mixture with air for Cu oxidation regulates the temperature in the reaction front, ensuring that undesirable hot spots that would lead to the irreversible loss of Cu activity are avoided. Since the gas/solid heat exchange front advances faster than the reaction front, the bed is eventually left at a low temperature. An additional stage was added to allow a gas/solid heat exchange between the hot recycled gas and the oxidized bed. This ensures that the fixed-bed is ready for the next reaction step that involves the reduction of CuO by a fuel gas. A sensitivity analysis of the main operating parameters confirms the theoretical viability of this operation. Cu oxidation is favoured at high pressure and therefore fast reaction rates were achieved, even with low contents of oxygen in the feed (around 3-4%). The recirculation of more than 80% of the exit gas from the oxidation reactor and its subsequent cooling down to around 423 K keep the maximum temperature down to within reasonable values (1173 K). Although this work was focused on the boundary conditions

of the Ca/Cu looping process for hydrogen production and/or power generation, some of the trends observed may be considered valid for other CLC systems that use similar N₂ recycles.

Keywords: Cu oxidation, adiabatic fixed-bed reactor, chemical looping, CO₂ capture, recycle

1. Introduction

The feasibility of using packed bed reactor technology to carry out Cu/CuO chemical loops at large scale has been evaluated in recent years [1-3]. With this technology, it is possible to generate a product gas at a high temperature and pressure that can be expanded in a gas turbine for power generation with high overall energy efficiency [4]. Cu-based oxygen carriers have a number of favorable features for chemical looping applications. These include high reaction rates for the reduction and oxidation stages, the absence of thermodynamic restrictions for the complete conversion of the fuel to CO₂ and H₂O, a high oxygen transfer capacity (0.5 moles of O₂/mole metal), a high resistance to carbon deposition, their relatively low cost and low environmental impact [5]. They also show good chemical and mechanical stability under repeated oxidation/reduction cycles, which is of great importance in processes involving fixed-bed reactors, in which the replacement of the solids can be costly. However, CuO has a relatively low melting point (1358 K) and therefore it cannot be used in the highest temperature range of CLC systems (1273-1473 K). Over 1223 K, Cu-based materials tend to agglomerate and their reactivity is drastically reduced [6]. Nevertheless, the choice of a suitable support and preparation method can considerably improve the performance of the solids, even under harsh operating conditions of pressure and temperature [7].

Careful control of temperature is required during the Cu oxidation stage in fixed bed reactors because of the high reaction enthalpy ($\Delta H_{298K} = -156$ kJ/mol). High temperatures in the reaction front could generate hot spots that would lead to an irreversible loss of Cu activity through agglomeration or volatilization. CLC systems in fixed beds are also attracting attention because of their potential application in novel Ca/Cu looping processes for hydrogen production and/or power generation [8]. This process involves an initial stage of sorption enhanced reforming

(SER) that provides a high hydrogen yield with a drastic reduction of CO₂ emissions since this gas is captured by CaO to produce CaCO₃. A Cu/CuO chemical loop is employed to carry out the regeneration of the CO₂ sorbent. The heat required for the calcination of the CaCO₃ formed in the SER step is supplied by the exothermic reduction of CuO by a fuel gas, which provides a product gas rich in CO₂ and readily separable H₂O. By coupling an endothermic and an exothermic reaction in the same solid matrix, a higher efficiency and lower equipment cost can be achieved, since the heat can be transferred directly from the pellets containing the metal to those containing the carbonate. In the Ca/Cu looping process, an even stricter control of the temperature is required [8], since the presence of calcium carbonate in the air reactor may lead to an unacceptable loss of CO₂ via the calcination of the sorbent at relatively low temperatures for a CLC system (above 1173 K).

Under these circumstances, and following the scheme of Fig. 1, the key parameters for regulating the maximum temperature achieved during the oxidation stage are: (1) the O₂ content in the gas fed into the reactor, (2) the inlet gas temperature, and (3) the average Cu/inert mass ratio in the solid bed. Low concentrations of oxygen, low gas temperatures and the high proportion of inert solids will moderate undesirable hot spots during the oxidation reaction. The product gas from the air reactor contains mainly nitrogen, which can be partially recycled after cooling in order to dilute the O₂ fed into the reactor. Since the flue gas is released at the highest allowable temperature in order to drive a gas turbine for power generation, it is necessary to include an intermediate heat exchange stage between Cu oxidation and CuO reduction to extract sufficient heat from the recycled gas before it is mixed with air at the exit of the air reactor, and at the same time to raise the temperature of the solids to a value that will allow the reduction of CuO to Cu in the next stage of the Ca/Cu looping process [8].

The purpose of this work is to simulate in detail the performance of an adiabatic fixed bed reactor during the Cu oxidation stage following the scheme of Fig. 1. A dynamic model incorporating existing knowledge on kinetics and basic assumptions about gas flow and heat

transfer within the fixed bed has been employed. The effect of the key design variables and operating conditions such as temperature, pressure, O₂ content in the feed, bed composition and Cu-based material reactivity was studied to demonstrate the theoretical viability of the process and to determine the operational window that would ensure optimal performance in terms of maximum flue gas temperature and minimum calcination of the sorbent. The implications of using a large recycling of N₂ to be mixed with air for Cu oxidation were also investigated. This work is essentially focused on the boundary conditions of the Ca/Cu looping process, but some of the data recorded and observed trends may be generally valid for other CLC systems that use similar N₂ recycling.

2. Mathematical model description

A pseudo-homogeneous model was developed to describe the Cu oxidation stage of a Ca/Cu looping process for hydrogen production on a large scale. This operation was described by means of a dynamic model, since the oxidation of Cu in a fixed-bed reactor is time-dependent, being the solids progressively converted during the operation. An adiabatic and multi-component system with a pressure drop and overall mass and energy balances were employed in the simulation. The following assumptions were adopted: an ideal plug flow pattern without axial dispersion, the absence of radial temperature or concentration gradients, negligible intraparticle concentrations and temperature gradients, ideal gas behavior, a constant bed void fraction and a uniform particle size in the oxygen carrier.

It is worth pointing out that at industrial scale these assumptions may be considered quite reasonable. Because of the high velocities expected (around 2 m/s), the reactor will perform at a high turbulent flow, which will allow a rapid mass and heat transfer between the gas and solid and a negligible dispersion of the gas throughout the reactor. According to the dispersion model proposed by Levenspiel [9] and taking into account the operating conditions listed in Table 1, the Peclet number ($Pe=uL/D_e$) can be expected to be higher than 3000, and therefore a plug flow pattern can be assumed in the Cu oxidation stage. For the conditions employed in this work, a

gas-solid heat transfer coefficient (h_{fs}) of about $300 \text{ W m}^{-2} \text{ K}^{-1}$ was obtained [11]. This value implies a very fast gas-solid heat exchange with no significant difference between the temperatures of the gas and solid at any point in the reactor. The mass transfer coefficient (k_{fs}) between the gas and the solid can be calculated by means of correlations analogous to those employed to estimate heat transfer coefficients. In this way, a gas-solid mass transfer coefficient of about 0.25 m s^{-1} was obtained [10]. Therefore, a rapid gas-solid mass transfer during the operation can be assumed, as reported by Breault [12].

A shrinking core mechanism with a plate-like geometry was employed to represent the kinetics of Cu oxidation, as is generally accepted in the literature on Cu-based materials in chemical looping applications. Although a more elaborate model has recently been published [13], the kinetics model obtained by García Labiano et al. [14] was chosen because it is simple and accurate and it fits the entire range of operating conditions considered in this work. When the chemical reaction is the main resistance to the global reaction, the following equations are used for the model:

$$\frac{t}{\tau} = X_{ox} \quad (1)$$

$$\tau = \frac{\rho_{m,Cu} L_{Cu}}{2 k_{ox} C_{O_2}} \quad (2)$$

where τ represents the time required for complete solid oxidation, X_{ox} is the solid conversion by oxidation, $\rho_{m,Cu}$ and L_{Cu} are the molar density and the layer thickness of the Cu-based material, respectively, k_{ox} is the chemical reaction rate constant of the Cu oxidation, and C_{O_2} is the concentration of oxygen in the gas phase. The values of the kinetics parameters are listed in Table 2.

According to Eqs. (1) and (2), the oxidation rate of the Cu-based solid and the consumption rate of O_2 during the operation ($\text{mol/m}^3\text{s}$) can be calculated respectively as follows:

$$r_{Cu} = \frac{\rho_{Cu} 1000}{M_{Cu}} \frac{dX_{ox}}{dt} \quad (3)$$

$$r_{N_2} = -\frac{r_{Cu}}{2} \quad (4)$$

where ρ_{Cu} is the apparent density of the Cu-based solid and M_{Cu} is the molecular weight of Cu.

Performance at high temperatures favours faster oxidation kinetics and higher energy efficiency, but it may also lead to a large loss of CO_2 from the calcination of $CaCO_3$. To describe the calcination kinetics of calcium carbonate, the model proposed by Martínez et al. [15] was chosen. According to this model, each carbonated particle is assumed to be made up of uniformly sized non-porous spherical grains of $CaCO_3$ that are calcined following a shrinking core model under chemical reaction control, Eq. (5).

$$\frac{dX_{calc}}{dt} = k_{calc}(1 - X_{calc})^{2/3}(C_{CO_2,eq} - C_{CO_2}) \quad (5)$$

The equilibrium concentration of CO_2 (mol/m³) can be estimated using Eq. (6) [16].

$$C_{CO_2,eq} = \frac{5.045 \cdot 10^{11}}{T} \exp\left(\frac{-20474}{T}\right) \quad (6)$$

The molar rate of CO_2 released per unit volume of sorbent, r_{CO_2} (mol m⁻³ s⁻¹) can be calculated from Eq. (7), where ρ_{CaCO_3} is the apparent density and M_{CaCO_3} is the molecular weight of $CaCO_3$, respectively.

$$r_{CO_2} = r_{calc} = \frac{\rho_{CaCO_3} 1000}{M_{CaCO_3}} \frac{dX_{calc}}{dt} \quad (7)$$

On the basis of the assumptions outlined above, the pseudo-homogeneous model of the differential mass balance for a packed bed can be written as:

$$s \frac{\partial C_i}{\partial t} = \frac{\partial(u C_i)}{\partial z} + \eta(1 - s)r_i \quad (8)$$

where C_i is the molar concentration of species i (O_2 , CO_2 , N_2), ε is the bed void fraction, u is the superficial velocity and η is the effectiveness factor. The last term on the right of Eq. (1) is zero for the N_2 mass balance because nitrogen acts as an inert component during the Cu oxidation process.

The pseudo-homogeneous energy balance for an adiabatic packed bed reactor according to a plug flow pattern can be expressed as:

$$\left[(1-\varepsilon) \rho_s c_{ps} + \varepsilon \rho_g c_{pg} \right] \frac{\partial T}{\partial z} = - \frac{\partial (u \rho_g c_{pg} T)}{\partial z} - (1-\varepsilon) \eta r_{O_2} \Delta H_{ox} - (1-\varepsilon) r_{calc} \Delta H_{calc} \quad (9)$$

where ρ_s is the average apparent density of the solids in the reactor, ρ_g is the gas phase density and c_{ps} and c_{pg} are the solid and gas heat capacities, respectively. ΔH_{ox} represents the heat of the Cu oxidation reaction and ΔH_{calc} represents the heat of the $CaCO_3$ calcination reaction.

The pressure loss ($MPa \cdot m^{-1}$) along the packed bed can be described by the Ergun equation as follows [17].

$$\frac{dP}{dz} = -[K_D u - K_V u^2] 10^{-6} \quad (10)$$

$$K_D = \frac{150 \mu_g (1-\varepsilon)^2}{d_p^2 \varepsilon^3} \quad (11)$$

$$K_V = \frac{1.75 (1-\varepsilon)}{d_p \varepsilon^3} \frac{M_g P}{0.062 T} \quad (12)$$

where P is the local pressure at the axial coordinate, K_D and K_V are the viscous and the kinetic pressure loss terms, u is the superficial velocity, μ_g is the viscosity of the fluid, ε is the bed porosity, d_p is the particle diameter. M_g is the molecular weight of the gas and T is the local temperature.

In packed-bed reactors, larger particles (pellets) must be used in order to moderate the pressure drop along the reactor during the operation. The effect of intraparticle mass-(and heat-) transfer limitations here may be considerable. As indicated above, the oxidation reactor, at the conditions listed in Table 1, performs at high turbulent flow and therefore the effect of external mass transfer on Cu oxidation reaction can be considered negligible. Internal diffusion limitations may appear in the case of large particles (i.e., those with a d_p higher than 0.001 m),

especially as a consequence of Knudsen diffusion [18]. However, important changes in the morphology of Cu-based materials were found after successive oxidation/reduction cycles, when they were carried out at high temperatures. Operating temperatures higher than 973 K cause a significant increase in the average pore size of Cu particles [19] and therefore the effect of diffusion limitations, even when the solid has undergone a high degree of conversion, may be partially reduced. Nevertheless, since the Ca/Cu looping process at large scale requires relatively large pellets (like those employed in industrial steam reforming), an effectiveness factor (η) was incorporated into the model. The value of the effectiveness factor is approximately constant during the Cu oxidation for a specific particle size, but it decreases considerably as the solid approaches its total conversion point [18]. In this work, an average effectiveness factor of about 0.3 was assumed in order to represent possible diffusion resistance in the pellets. This assumption is in agreement with the results recently published on Cu oxidation for chemical looping applications [13, 18].

The choice of reactor length and the superficial gas velocity per unit reaction area must be a trade-off between the gas-solid contact time requirements and the maximum allowable pressure drop along the reactor. For this preliminary design stage, a reactor length of 7 m and an inlet mass flow velocity of about $0.85 \text{ kg m}^{-2} \text{ s}^{-1}$ of oxygen was adopted. This would correspond to a Ca/Cu looping plant of 500 MW_t with a maximum pressure drop during each Cu/CuO cycle of around 0.1 MPa [8]. These parameters allow reasonable cycle times and lead to sharp breakthroughs during the Cu oxidation stage. This study has been focused on the Cu oxidation carried out at high pressures (1 MPa-3.5 MPa) and temperatures (823 K-1100 K), which are the conditions that ensure optimal performance in the Ca/Cu looping process [8]. Under these operating conditions, Cu oxidation is complete [13] and fast oxidation rates are achieved even with low contents of oxygen in the gas phase. The composition of the bed reactor (see Table 1) is a consequence of the conditions required for carrying out the overall Ca/Cu process. An appropriate Cu/Ca proportion and a reforming catalyst are needed to ensure that all the reactions involved take place in the different reaction stages (Fig. 1), as reported in previous works [20,

8]. The content of Cu and CaCO_3 in the solid bed for the reference case is around 28 wt.% and 23 wt.%, respectively. The rest of bed composition corresponds to the sum of inert support of both Cu- and Ca-based materials, the inert CaO present in Ca-based sorbents, and the reforming catalyst (<8 wt.%) required for the previous SER stage. The effects of possible changes in the oxidation state of the reforming catalyst during the Cu oxidation stage were considered negligible in this work.

As explained above, the mathematical model is mainly composed of partial differential equations, algebraic equations, and initial and boundary conditions. The model was implemented and solved using MATLAB programming software. The partial differential equations, Eq. (8) (one for each component $i = \text{O}_2, \text{N}_2, \text{CO}_2$) and Eq. (9) were converted to a set of ordinary differential equations with initial conditions by discretizing the spatial derivative in axial direction (z) using backward finite differences.

The initial and boundary conditions in Eqs. (8), (9) and (10) are as follows:

$$C_i = C_{i,0} \quad T = T_{s0} \quad \text{at } t=0 \quad (13)$$

$$C_i = C_{i, \text{in}} \quad T = T_{g, \text{in}} \quad P = P_{\text{in}} \quad \text{at } z=0 \quad (14)$$

The initial concentrations of the gas species in the reactor should be set to zero, but they were actually considered as equal to 10^{-6} in order to avoid denominators equal to zero in the equations described above. The system formed by the ordinary differential equations and the other algebraic equations mentioned above were simultaneously solved employing the “ode15s.m” function, which is a MATLAB tool for solving initial value problems in stiff ordinary differential equations.

A summary of the reactor characteristics and operating conditions used in the reference case is provided in Table 1. These together with the initial and boundary conditions of Eqs. (13-14) make it possible to obtain a complete solution for the dynamic model.

3. Dynamic analysis of the fixed bed reactors during Cu oxidation

The previous model was designed to analyze the dynamic evolution of the concentrations of O₂, N₂ and CO₂ in the axial direction of an adiabatic fixed-bed reactor. By means of this model it is possible to determine the axial concentration and temperature profiles along the reactor in terms of time and to predict the breakthrough time in accordance with the operating conditions outlined in Table 1. The high Cu oxidation enthalpy requires a highly diluted O₂ gas stream to be fed into the air reactor at a low temperature (around 423 K). This involves the recirculation and cooling down of a large part of the exit gas in order to moderate the maximum adiabatic increase of temperature during the operation (Fig. 1). With a recycle ratio (R) of around 0.85, it is possible to reduce the O₂ content in the gas feed by as much as 3.6%. According to the conditions presented in Table 1, the mass flow velocity is 21 kg m⁻²s⁻¹, which implies a gas velocity close to 2 m s⁻¹.

As the gas stream passes through the bed, the concentration of O₂ gradually decreases while the solid approaches total oxidation. The high operating pressures required to carry out the Cu oxidation stage within the Ca/Cu looping process (higher than 1 MPa), facilitate very fast oxidation rates even with a very low amount of O₂ in the oxidizing stream. Under the operating conditions listed in Table 1, a starting temperature in the bed of about 923 K permits, from the very beginning, the rapid and total conversion of oxygen in a narrow reaction front (see Fig. 2a and Fig. 2c). The gas, that arrives at the reaction front at the inlet temperature (T_{gin}), quickly heats up because of the exothermicity of Cu oxidation reaction ($\Delta H_{298K} = -156$ kJ/mol) and advances towards unconverted solids, which are at a lower temperature. The heat thus generated is transported downstream, heating the solids up to above their initial temperature of 923 K (T_{s0}). In this way, the oxidation front gradually raises the temperature of the bed as it moves towards the reactor exit, until a maximum temperature of about 1100 K is reached (Fig. 2d). The speed at which both fronts move towards the exit depends on the properties of the solid and gas phases and on the concentrations of the reactants [1, 8]. Due to the low oxygen content in the gas phase, the heat exchange front advances much faster than the reaction front. As can be seen in Fig. 2c and Fig. 2d, after 600 s of operation, the reaction front has advanced around 4.5 m (of

7 m of reactor length), while the flue gas is discharged at around 1070 K (close to the maximum temperature of the oxidation stage), which indicates that at that time the heat reaction front has almost reached the exit of the reactor. Since the heat exchange front moves ahead the CuO formed in the reaction front is cooled down by the incoming gas at its inlet temperature (423 K) and this temperature is too low to initiate the next reaction stage of the Ca/Cu looping process, which involves the reduction of the CuO to Cu by a fuel gas. Therefore, an additional heat exchange stage is required, as mentioned above. The consequences of using a large N₂ recycling together with this additional stage are discussed later.

The Cu oxidation stage can be divided into three periods according to the evolution of the gas composition and the temperature at the exit of the bed reactor (Fig. 3). During the prebreakthrough period ($t < 1000$ s) the oxygen is totally converted, despite the high space velocity and the low content of O₂ in the gas phase. During the first part of this period ($t < 400$ s), the heat exchange front is still inside the reactor and the flue gas temperature is close to the starting temperature of the solids (923 K). When this front approaches the exit, the temperature profile gradually increases until it reaches a maximum of about 1100 K. By the time the flue gas leaves the reactor at 923 K, it is basically composed of nitrogen because at this temperature the calcination is negligible. However, as the temperature increases ($t > 400$ s), the content of CO₂ in the product gas also increases until it reaches a maximum of around 1%, which corresponds to the value given by the equilibrium for the calcination reaction at 1100 K. Since the solid bed was initially composed of 23% of CaCO₃ (Table 1), only 4% of the carbonate will be calcined during the Cu oxidation stage.

When the solids bed is almost completely oxidized (i. e., the reaction front is close to the exit), the content of O₂ in the flue gas gradually increases ($t > 1000$ s) from 0% to 3.6% (breakthrough period). Due to the rapid Cu oxidation, a short breakthrough period is observed (at around 300 s), which is highly favorable in operations carried out in alternative fixed-bed reactors. In order to maximize the global efficiency of the process, a valve setup must be used to guide the product gas to the turbine during the period of time in which it is emitted at higher

temperatures. The rest of the flue gas (85%) will be recirculated and used in an intermediate stage to raise the temperature of the depleted solids bed before the reduction stage begins.

The evolution of the solids bed and flue gas temperature during this solid/gas heat exchange step is represented in Fig. 4. As pointed out above, there is an initial period ($t < 400$ s) in which the recirculated gas is fed into the oxidized bed at 923 K (T_{s0} of the oxidation stage). As the gas stream passes through the bed, all of the sensible heat is transferred from the gas to the solids and the temperature of the bed gradually increases. During this period of time, the flue gas abandons the reactor at 423 K before it is mixed with an air stream that comes from a compressor for Cu oxidation. The second period of this stage lasts up to 900 s, depending on the duration of the oxidation stage and the recirculation ratio (0.85, as mentioned above). The temperature of the recirculated gas gradually increases from 923 K to nearly 1100 K (Fig. 3) which means that most of the oxidized bed is heated up to above 923 K, as can be seen in Fig. 4. At the end of this stage, the solids bed shows a temperature profile ranging from 1100 K at the reactor inlet to 940 K at the reactor exit. These conditions allow the next stage of the Ca/Cu looping process to be initiated. This involves the Cu reduction, coupled with the calcination of the CO₂ sorbent. Since the temperature of the feed gas in the oxidation stage needs to be around 423 K (Table 1), an additional heat exchanger is required downstream of the second bed reactor in order to remove any excess of sensible heat in the recirculated gas before it is fed back into the air reactor.

4. Sensitivity analysis

The effect of the key design variables and operating conditions on Cu oxidation in an adiabatic fixed bed reactor was studied in detail in order to demonstrate the theoretical viability of this process on a large scale. In addition, the operational window that ensures optimal performance in terms of energy and CO₂ capture efficiency within the boundary conditions of the Ca/Cu looping process was determined. Once a set of reactor characteristics and operating conditions had been defined (Table 1), a simulation of the air reactor performance (Fig. 1) was

carried out to investigate the effects of temperature, pressure, Cu content in the bed, solid reactivity and O₂ content in the feed together with the implications of using a large recycling of N₂ that will be mixed with air for the oxidation of Cu.

4.1. Effect of temperature

As previously mentioned, strict control of the temperature is required during the highly exothermic Cu oxidation when it is carried out in an adiabatic fixed-bed reactor. The main parameters for regulating the maximum temperature achieved during the oxidation stage are the temperature of the inlet gas and the initial temperature of the solids bed. In this study, the effect of both variables was investigated separately. In conventional CLC systems, the oxidation reaction must be carried out at the highest allowable temperature in order to maximize energy efficiency by means of the expansion of the flue gas in a turbine. In the Ca/Cu looping process, the main source of energy is the H₂ obtained in the SER stage, whereas the potential energy that can be obtained from the flue gas in a gas turbine is very low (around 30 MW_e in a 400 MW_e power plant). However, high temperatures during Cu oxidation are highly desirable in order to heat up with the recycle (Fig. 1) a large part of the solid bed up to favorable conditions for the Cu reduction stage, and so enhance the overall efficiency of the process [8].

The composition (N₂ is not shown) and the temperature of the product gas during the Cu oxidation process is represented in Fig. 5 for different inlet gas temperatures (from 423 K to 523 K) when the Cu oxidation is carried out by feeding 21 kg/m²s of inlet gas (3.6% O₂ content) at 423 K (T_{gin}) and at 3.5 MPa. The results of the simulation show that higher a T_{gin} leads to shorter breakthrough periods because the kinetics of Cu oxidation are favored at high temperatures. During the first 400 s, all the temperature profiles match each other and are equal to the initial solids temperature (923 K). However, for longer operation times (as the reaction front moves forward and approaches the reactor exit) the temperature profiles are largely affected by T_{gin}. At 423 K, the temperature increases gradually up to a maximum of about 1100

K at the end of the prebreakthrough period. This low inlet temperature and the high operating pressure (3.5 MPa) minimize the calcination of CaCO_3 (at most 1% of CO_2 in the product gas). If the inlet gas is fed in at 523 K, the temperature of the product gas rapidly escalates to a maximum of about 1165 K, where it remains while the solids are not close to complete oxidation. On the other hand the amount of recycled N_2 at this maximum temperature increases, making it possible to heat a larger part of the solids bed up to favorable conditions for the Cu reduction stage (Fig. 1). However, these conditions lead to a lower CO_2 capture efficiency because at this maximum temperature, the flue gas achieves a CO_2 content of about 2.5 % and approximately 12% of the carbonate present in the bed is calcined during the Cu oxidation operation.

The initial temperature of the solids (T_{s0}) was also evaluated in order to study its effect on the temperature of the flue gas and therefore on the temperature profile during the subsequent solid/gas heat exchange stage. This temperature directly depends on the conditions chosen to carry out the SER stage that take place before the oxidation step during the Ca/Cu looping process. The final temperature of SER stage is strongly affected by the inlet gas temperature and the S/C molar ratio fed into. An initial temperature of around 823 K is sufficiently high to promote from the very beginning a rapid Cu oxidation, but this value can be significantly higher. Moreover, a flat temperature profile at the beginning of oxidation stage is possible when the previous SER stage is carried out by feeding high S/C molar ratios (>5) and using CO_2 sorbents with high content of active phase (which are in fact the most favourable conditions for a SER operation). Under these circumstances, both reaction and heat exchange fronts will advance very close and therefore, at the end of the SER stage, the temperature of the solids is similar along the packed bed. In contrast, if the active content in the sorbent and/or the S/C molar ratio in the feed are low, the reaction front will advance much faster than the heat exchange front, and therefore the bed will be finally divided in two zones at different temperatures. For the purpose of this work, we have considered at the beginning of the Cu oxidation stage a uniform temperature profile.

The influence of the initial temperature of the solids bed (from 823 K to 1023 K) on the composition and temperature evolution at the exit of the oxidation reactor is shown in Fig. 6. Total O₂ conversion is achieved during the prebreakthrough period even at the lowest T_{s0} tested (823 K). During the first 500 s, the heat exchange front is still inside the reactor, the temperature of the flue gas depends exclusively on T_{s0} and therefore the temperature profiles differ markedly. However, once the heat front has reached the exit and during the period of time in which the reaction front moves along the bed, the product gas gradually increases its temperature to a maximum of around 1100 K for all the T_{s0} tested. The results show that the maximum temperature is exclusively determined by the temperature of the inlet gas (T_{gin}) and by the maximum adiabatic temperature increase ($\Delta T_{\max}$), and not by the initial temperature of the solids, as previously reported by Fernandez et al. [8].

4.2. Effect of pressure

As mentioned above, the use of packed bed reactor technology in processes intended for power generation makes it possible to operate at high pressure and therefore achieve a high overall efficiency [4, 20, 21]. In the case of the Ca/Cu looping process, performance at high pressure leads to faster reaction rates during the Cu oxidation stage and also reduces the loss of carbon through CaCO₃ calcination, even at relatively high operating temperatures [22]. The Ca/Cu looping process can be carried out at very different pressures depending on its final purpose. When it is exclusively focused on power generation, the H₂ obtained in the SER stage is burned in the gas turbine of a Combined Cycle and therefore the operating pressure must be around 1.8-2 MPa. However, when the main objective is the H₂ production, the SER and the Cu oxidation stages must be carried out at the usual pressures of conventional steam methane reforming (higher than 3 MPa). The integration between the Ca/Cu looping process into a NGCC for electricity production was studied by Martinez et al. [23], and the design of a H₂ production plant based on the Ca/Cu chemical looping process was evaluated by Martinez et al. [24]. In the present study, the dynamic behavior of the oxidation reactor was investigated at different operating pressures (from 1 MPa to 3.5 MPa).

Fig. 7 shows that Cu oxidation is favored by high operating pressures, which allow fast kinetics even when there is a low content of oxygen present in the inlet gas (3.6 %). Performance at 3.5 MPa leads to a sharp breakthrough, which is highly desirable in operations carried out in alternative fixed-bed reactors. The stationary period, in which total oxygen conversion take place, can be extended to 1000 s by employing a pressure of 3.5 MPa, with a breakthrough period of about 300 s. However, at the lowest pressure tested (1 MPa), the breakthrough period starts after 800 s of operation, and it lasts for more than 700 s before the bed is totally oxidized.

The content of CO₂ in the flue gas was considerably reduced when the process was performed at a higher pressure and therefore CO₂ capture efficiency improved. The maximum CO₂ concentration in the product gas increased from 1%, at 3.5 MPa, to 1.8% at 1 MPa. Under these circumstances, in a solid bed initially composed of 23% of CaCO₃ (Table 1), the proportion of carbonate calcined during the Cu oxidation stage would be 4% at 3.5 MPa and 8% at 1 MPa.

The evolution of the temperature of the flue gas was similar at all the pressures tested. However, it was found that higher operating pressures lead to higher maximum temperatures, because the Cu oxidation reaction rate is promoted (exothermic) whereas the calcination of CaCO₃ is significantly reduced (endothermic). Consequently the flue gas during the second half of the prebreakthrough period is released at higher temperatures (see Fig. 7), maximum temperatures of 1100 K and 1068 K being reached at 3.5 MPa and 1 MPa, respectively. Thus oxidation at high pressure is desirable, since Cu oxidation is favored, the flue gas is released at higher temperatures and the loss of carbon from the calcinations of carbonate is minimal, which leads to a rise in CO₂ capture efficiency.

4.3. Effect of Cu-based solid reactivity

The reactivity of the Cu-based material can play a decisive role in the overall efficiency and viability of the Cu oxidation stage within the boundary conditions of the Ca/Cu looping process.

The effect of using Cu-based materials with a considerably lower reactivity on the composition of the flue gas and temperature profiles has also been evaluated.

Fig. 8 shows that the total conversion of oxygen can be achieved by using a less reactive Cu-based material with a quarter of the reactivity reported by García Labiano et al. [14]. However, less reactive materials do not produce sharp breakthroughs, which means that longer periods of operation are needed before complete bed oxidation is achieved. As pointed out above, the breakthrough period, assuming a high reactivity ($k_{0,ox}=4.7 \cdot 10^{-6}$ m/s), starts after the first 1000s of operation and only lasts 300 s before the bed is totally oxidized. With a much less reactive material ($k_{0,ox}/4$), the breakthrough is prolonged by more than 800 s and therefore the Cu oxidation stage is not completed until after 2000 s of operation.

The temperature profiles of the flue gas are also affected by the reactivity of the Cu-based material. If the Cu oxidation is very slow, this exothermic reaction proceeds more gradually and the result is a slight increase in the flue gas temperature during the Cu oxidation operation. The maximum temperature achieved during the operation is 1010 K for the lowest reactive material tested, whereas T_{max} increases to 1100 K if the most reactive solid is used. Therefore, slow-reacting Cu-materials produce a lower temperature rise during oxidation and, as a consequence, lower energy efficiencies are obtained. However, the calcination of $CaCO_3$ is minimized and a very high CO_2 capture efficiency is achieved. The possible loss of reactivity of Cu-based materials after many redox cycles would therefore allow a higher content of O_2 to be fed in with the inlet gas without reaching the high temperatures that lead to excessive $CaCO_3$ calcination or Cu agglomeration. Cu oxidation could then be carried out with lower recirculation ratios (see Fig. 1) and therefore less piping requirements and lower blowing costs.

4.4. Effect of Cu content on the solids bed

Functional materials with the right proportions of Cu and CaO are necessary to carry out the Ca/Cu looping process and ensure that all the reactions involved take place in the different reaction stages. The type of fuel gas employed to regenerate the CO_2 sorbent in the final stage of

the Ca/Cu looping process will determine the proportion of Cu required in the solid bed [22]. Therefore, the Cu oxidation stage can be carried out with different amount of Cu in the matrix bed and the operational window for optimal performance will be affected.

Fig. 9 shows the dynamic behaviour during the Cu oxidation stage for different Cu contents in the solids bed (from 23% to 33%), at the boundary conditions summarized in Table 1 for a Ca/Cu looping process. Higher amounts of Cu in the bed gradually extend the duration of the prebreakthrough period from 840 s, with 23% of Cu, to 1100 s, with 33% of Cu. Moreover, higher temperatures during operation are promoted and therefore the loss of CO₂ through calcination will increase. When the Cu content is increased from 23% to 33% the maximum temperature of the flue gas increases from 1070 K to 1125 K. In these conditions, the presence of CO₂ in the product gas rises from 0.5% to 1.4%, respectively. Furthermore, by increasing the amount of Cu in the bed, the proportion of product gas discharged at maximum temperature is considerably higher. As a result, although the energy efficiency of the process is greater, the CO₂ capture efficiency is significantly reduced. In a solid bed initially composed of 23% CaCO₃, with a Cu content of 23%, only 2.5% of the carbonate will be calcined. However, with a Cu content of 33%, the proportion of carbonate calcined will increase to 9%. Therefore, having a reasonable proportion of Cu in the solid bed is essential for achieving a high energy efficiency with minimal calcination of CaCO₃.

4.5. Effect of O₂ content in the feed

The proportion of O₂ in the feed has a substantial effect on Cu oxidation and determines the operational window in the air reactor. A high concentration of O₂ in the feed allows fast oxidation kinetics (Eq. 2), but it may promote an excessive increase in temperature in the reaction front and therefore a considerable loss of CO₂ capture efficiency. A reasonable recirculation ratio (R) has to be found in order to ensure fast oxidation kinetics and a high energy efficiency with minimal CaCO₃ calcination. Fig. 10 shows the dynamic behaviour of the air reactor during the Cu oxidation stage for different inlet O₂ contents, from 3% to 4%, which

involves recirculation ratios between 0.87 and 0.83 respectively, for the boundary conditions summarized in Table 1.

Fig. 10 shows that it is possible to achieve an O₂ content of around 3% with a recycle ratio of around 0.87. Despite the large mass flow velocity (24 kg/m²s) and the low concentration of O₂ in the gas phase, a total conversion is attained during the prebreakthrough period ($t < 1000$ s). The Cu oxidation is relatively fast and the breakthrough period takes place approximately between 1000 s and $t = 1500$ s. The maximum temperature in the flue gas (i. e. approximately 994 K) occurs at the end of the prebreakthrough. This low temperature together with the high operating pressure (3.5 MPa) minimize CaCO₃ calcination (at most 0.13% of CO₂ in the product gas). With a recycle ratio of around 0.83, an O₂ concentration of about 4% is obtained in the feed gas. Under these circumstances, the breakthrough period is significantly shorter (from $t = 1000$ s to $t = 1200$ s) and a flue gas with a maximum temperature of about 1173 K is produced during the second half of the prebreakthrough. However, CO₂ capture efficiency drops, because at this maximum temperature the content of CO₂ in the flue gas is nearly 3%. In a solids bed initially composed of 23% of CaCO₃ (Table 1), approximately 20% of the carbonate will be calcined during the Cu oxidation stage. Thus the high reaction enthalpy of the Cu oxidation reaction makes it necessary to feed in a very low O₂ content in order to moderate the temperature rise during operation. Since slight variations in the O₂ content give rise to large temperature increases, Cu oxidation must be carried out in a very narrow operational range.

The effect of the O₂ content on the increase of temperature in the reaction front is significantly higher when the concentration of O₂ is changed by regulating the recirculation ratio, because the total flow to the air reactor is also changed. If the O₂ content varies but the total flow to the air reactor is maintained, the velocity of the reaction front changes while the velocity of the heat front is the same [18]. As explained above, a large recirculation ratio is required in the Ca/Cu process in order to feed a low O₂ content into the air reactor. In this case, there is a large increase in the total gas flow to the reactor and therefore the velocity of the heat exchange front is much higher than the reaction front. There will be more solids between both

fronts that can absorb the heat from the oxidation reaction and therefore the increase of temperature is lower. In contrast, when the content of O_2 is higher, the recirculation ratio must have been highly reduced and therefore both fronts advance closer. There are fewer solids between both fronts to accommodate the heat from the reaction and therefore the increase of temperature is much higher.

Regarding the additional solid/gas heat exchange stage, the results are strongly conditioned by the operating conditions chosen for the previous Cu oxidation stage (see Fig. 1). A higher O_2 content in the feed of the air reactor means that a smaller amount of gas is recirculated, but at a higher temperature. A representation of the final solid bed temperatures and flue gas temperature profiles during this solid/gas heat exchange step is provided in Fig. 11, for different inlet O_2 contents (from 3% to 4%, that involve recirculation ratios from 0.87 to 0.83, respectively). When 3% of O_2 is fed into the oxidizing reactor, a large recirculated ratio of about 0.87 is required, as mentioned above. Therefore, a large amount of gas is available for raising the oxidized bed before undertaking the subsequent CuO reduction stage, but it is emitted at a relatively low temperature. As a result, the oxidized bed heats up to temperatures slightly higher than 923 K, reaching a maximum temperature at the inlet of bed reactor of about 990 K. During the first 250 s of the operation, the flue gas transfers all the sensible heat to the solids and it is released at 423 K. Once the temperature of the bed increases and the heat exchange front approaches the reactor exit, the temperature of the flue gas progressively increases up to 935 K. The excess of sensible heat is removed in an additional heat exchanger downstream (see Fig. 1), because the recirculated gas needs to be around 423 K before it is fed back into the air reactor. If 4% of O_2 is fed into the air reactor, a smaller amount of gas is available for the heat exchange stage ($R=0.83$), but at considerably higher temperatures. In these conditions, nearly half of the oxidized bed is heated up to around 1170 K, which is highly favorable for carrying out the CuO reduction stage. Since the mass flow velocity is lower, the heat exchange front advances more slowly and therefore, the flue gas is emitted at 423 K for a longer period of time ($t < 360$ s). This means that less sensible heat needs to be removed in the heat exchanger downstream.

Conclusions

A dynamic model developed to describe the transient performance of the oxidation of a Cu-based material in an adiabatic fixed-bed reactor, confirms the theoretical viability of this reaction stage within the boundary conditions of the Ca/Cu looping process. Operating parameters, such as the temperature and composition of the gas feed, initial solids temperature, pressure, bed composition and recirculation ratio were found to have a substantial effect on performance in terms of energy efficiency and CO₂ capture efficiency. A significant fraction of the exit gas from the air reactor must be recycled (higher than 0.83) and cooled down to around 423 K in order to regulate the temperature in the Cu oxidation front and limit the maximum temperature to reasonable values (below 1173K). Cu oxidation is favoured at high pressure and therefore fast reaction rates can be achieved in the high temperature reaction front even with low contents of oxygen (around 3-4%) in the feed. It has been demonstrated that the resultant residence time of the gas inside the oxidation reactor allows total oxygen conversion to take place, so that the flue gas will be composed mainly of nitrogen. The additional gas/solid heat exchange step allows the excess of heat to be transferred from the recycle gas to the oxidized bed, which will increase the solid temperature up to values (generally above 1000K) suitable for the subsequent reduction of CuO.

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Nomenclature

C_i	concentration of component 'i' in the reactor, mol m ⁻³
C_{pg}	heat capacity of the gas, kJ kg ⁻¹ K ⁻¹
C_{ps}	heat capacity of the solid, kJ kg ⁻¹ K ⁻¹
C_{O_2}	concentration of O ₂ in the gas phase, mol m ⁻³
$C_{O_2,eq}$	equilibrium concentration of CO ₂ , mol m ⁻³

$C_{i,in}$	concentration of component i in the feed, mol m^{-3}
$C_{i,0}$	initial concentration of component i, mol m^{-3}
d_p	particle diameter, m
D_e	effective diffusivity, $\text{m}^2 \text{s}^{-1}$
E_a	activation energy, kJ mol^{-1}
ΔH_{calc}	heat of CaCO_3 calcination, kJ mol^{-1}
ΔH_{ox}	heat of Cu oxidation, kJ mol^{-1}
h_{fs}	fluid-gas heat transfer coefficient, $\text{W m}^{-2} \text{K}^{-1}$
k_{calc}	reaction rate constant of the CaCO_3 calcination, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$k_{0,\text{calc}}$	preexponential factor of the CaCO_3 calcination reaction rate constant, $\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
$k_{0,\text{ox}}$	preexponential factor of the Cu oxidation reaction rate constant, m s^{-1}
k_{ox}	reaction rate constant of the Cu oxidation, m s^{-1}
k_{fs}	fluid-gas mass transfer coefficient, m s^{-1}
L	reactor length, m
L_{Cu}	layer thickness of Cu, m
M_{CaCO_3}	molecular weight of CaCO_3 , kg kmol^{-1}
M_{Cu}	molecular weight of Cu, kg kmol^{-1}
M_g	molecular weight of the gas, kg kmol^{-1}
P	total pressure, MPa
P_i	partial pressure of component i, MPa
P_{in}	pressure at the reactor entrance, MPa
r_{calc}	calcination rate of CaCO_3 , $\text{mol m}^{-3} \text{s}^{-1}$
r_{CO_2}	formation rate of CO_2 , $\text{mol m}^{-3} \text{s}^{-1}$
r_{Cu}	rate of oxidation of the Cu-based solid, $\text{mol m}^{-3} \text{s}^{-1}$
r_{O_2}	consumption rate of oxygen, $\text{mol m}^{-3} \text{s}^{-1}$
R	recirculation ratio, dimensionless
t	time, s

T	temperature, K
T_{gin}	feed gas temperature, K
T_{s0}	initial temperature of the solids in the reactor, K
u	superficial velocity of gas, m s^{-1}
X_{calc}	fractional calcination conversion of CaCO_3 , dimensionless
X_{ox}	fractional oxidation conversion of Cu, dimensionless
z	axial coordinate in bed, m

Greek letters

ε	bed void fraction, dimensionless
ρ_{CaCO_3}	apparent density of CaCO_3 , kg m^{-3}
ρ_{Cu}	apparent density of Cu-based material, kg m^{-3}
ρ_{g}	gas phase density, kg m^{-3}
$\rho_{\text{m,Cu}}$	molar density of Cu, mol m^{-3}
ρ_{s}	apparent density of the mixed solids in reactor, kg m^{-3}
η	effectiveness factor, dimensionless
τ	time for complete solid conversion, dimensionless

μ_{g}	gas viscosity, MPa s
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Figure Captions

Fig. 1. Scheme of the Cu oxidation stage in a CLC system with a large recycle of N_2 .

Fig. 2. Dynamic profiles of O_2 , CO_2 , solid conversion and temperature in an adiabatic fixed-bed reactor during the Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.5 MPa, 3.6% O_2).

Fig. 3. Product gas composition and temperature evolution of the gas leaving the oxidation reactor with time (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.5 MPa, 3.6% O_2).

Fig. 4. Temperature profiles of the solids bed and flue gas during the additional solid/gas heat exchange stage.

Fig. 5. Effect of inlet gas temperature on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 923 K (T_{s0}), 3.5 MPa, 3.6% O_2).

Fig. 6. Effect of initial solids bed temperature on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 3.5 MPa, 3.6% O_2).

Fig. 7. Effect of pressure on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.6% O_2).

Fig. 8. Effect of Cu-based solid reactivity on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.5 MPa, 3.6% O_2).

Fig. 9. Effect of Cu content in the solid bed on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.5 MPa, 3.6% O_2).

Fig. 10. Effect of O_2 content (and recirculation ratio) on the composition and temperature of the exit gas during Cu oxidation (under the conditions shown in Table 1: 423 K (T_{gin}), 923 K (T_{s0}), 3.5 MPa).

Fig. 11. Effect of O_2 content (and recirculation ratio) on temperature profiles of the solids bed and flue gas during the additional solid/gas heat exchange stage.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

Fig. 10

Fig. 11

Table 1. Operating conditions and reactor characteristics corresponding to the reference case study.

Parameters	Values
Feed gas temperature, T_{gin}	423 K
Initial solids temperature, T_{s0}	923 K
Pressure	3.5 MPa
Inlet mass flow velocity	$21 \text{ kg m}^{-2} \text{ s}^{-1}$
Inlet O_2 concentration	3.6%
η	0.3
d_p	0.01 m
L	7 m
ε	0.5
ρ_{Cu}	950 kg m^{-3}
ρ_{CaCO_3}	785 kg m^{-3}
ρ_s	3400 kg m^{-3}

Table 2. Kinetic parameters of reactions involved in this work.

Parameters	Values
$\rho_{\text{m,Cu}}, \text{ mol m}^{-3}$	140252
$L_{\text{Cu}}, \text{ m}$	$2.3 \cdot 10^{-10}$
$k_{\text{o,ox}}, \text{ m s}^{-1}$	$4.7 \cdot 10^{-6}$
$E_{\text{a,ox}}, \text{ kJ mol}^{-1}$	15
$k_{\text{o,calc}}, \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$	252.015
$E_{\text{a,calc}}, \text{ kJ mol}^{-1}$	91.7