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An Empirical Kinetic Model of a Stone Dust Looping Carbonator for Ventilation Air Methane Abatement

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ABSTRACT

A novel stone dust looping (SDL) process for mitigation of ventilation air methane (VAM) was investigated. The SDL process uses limestone as a sorbent to capture CO₂ emissions, similar to a conventional calcium looping (CCL) process. However, unlike CCL where lime (CaO) is introduced directly to a flue gas from a thermal power plant with CO₂ concentrations as high as 12-15% in an oxygen deficient environment; the SDL process uses CaO to catalytically oxidise VAM, with concentrations of CH₄ up to 0.1 to 1 vol. % in air, and simultaneously capture CO₂ produced. In the present study kinetic parameters were derived from experiments in a single lab scale fluidised bed reactor. A random pore model (RPM) was used to determine the rate controlling steps for the SDL process and kinetic parameters such as activation energy (E_{aK}) and pre-exponential factor (k_{s0}) were obtained for an SDL process carbonator. Kinetic parameters were then used to derive an empirical model for a continuous SDL process and consisted of residence time distribution functions, sorbent kinetics and deactivation rate. The empirical model has the ability to simulate and predict various operating and design conditions under which the real SDL process will operate. From the model, the optimum bed inventory, solid circulation rates and stone dust makeup rates have been calculated to achieve the desired CO₂ capture efficiency.

1. Introduction

Ventilation air methane (VAM) is a dilute stream of methane, typically at concentrations < 1 vol% CH₄, contained in large ventilation air streams exiting underground coal mines. VAM is the result of the large amount of air required, approximately 100-300 m³/s, to dilute CH₄

liberated from the working face of a coal seam in an underground coal mine in order to ensure CH₄ concentrations are below its lower explosive limit (LEL) of 5 vol%. Fugitive emissions resulting from VAM^{1, 2} are of an environmental and economic concern at underground coal mining operations in Australia. This stems from the fact that the global warming potential (GWP) of CH₄ is 25 times that of CO₂. One method to combat VAM emissions is to oxidise the CH₄ in VAM to CO₂ resulting in approximately a 9 times reduction in carbon emissions on a weight basis. Also, CH₄ in VAM, although in dilute concentration, is considered to be a potential energy source that can be used for heat or power generation. However, the dilute nature of methane in VAM and the extremely high flowrates, make VAM very arduous to process via conventional technologies such as thermal oxidisers, gas engines and gas turbines. The primary pitfall of thermal oxidiser technology is the high operating temperature (>1000°C) and the associated safety concerns of such high temperatures on a mine site^{1, 3, 4}. On the other hand, gas engines and turbines need higher amounts of auxiliary fuel that may add significant cost to the VAM abatement operation³.

Considering the associated issues with current and emerging VAM abatement technologies, a novel stone dust looping (SDL) process is being developed at the University of Newcastle as part of larger chemical/calcium looping program⁵⁻¹⁸ to thermally oxidise VAM in addition to capturing CO₂ produced from this reaction. As the primary issue with all VAM abatement technologies is their integration with the coal mining shaft, the advantage of the SDL process is that it can reduce some of the associated safety concerns in comparison to conventional thermal oxidisers. Thermal oxidiser technologies pose a significantly higher risk as they operate in the region of ~900-1000°C, whereas the carbonator unit in the SDL process, which will receive the VAM stream, operates at 450-650°C. This is of significant benefit for mine site integration as the heat flux that is required to be reduced, in terms of providing passive safety measures (i.e. water spray), is 35-60% less than that of conventional thermal oxidiser technologies.

A further advantage of the SDL process is that it is the only VAM abatement process that can provide the option of zero emission mining. That is, based on the carbon market situation, the SDL process can be designed in one of two basic versions: 1. the CO₂ capture / drainage gas integration design or 2. the no CO₂ capture/ no drainage gas integration design. The latter design needs to be operated at temperatures between 620-650 °C while the former design operates at temperatures of 450-620 °C. The no CO₂ capture/ no drainage gas integration design does not require a two reactor configuration (i.e. the carbonator and calciner) and can be executed in a

single reactor. This is because the process will be operated at conditions where the actual partial pressure of CO_2 in the reactor is higher than the equilibrium partial pressure of CO_2 which ensures that no CO_2 is captured by CaO . Therefore, no calciner and hence no drainage gas will be required. In this configuration and at the operating temperatures of 620- 650 °C a 35-38% reduction in the operating temperature over conventional thermal oxidiser technology is still obtained. In the case of the CO_2 capture/ drainage gas integration design, where a calciner is used, a mechanical loop seal is provided between the two fluidised beds which negates the risk of the VAM stream travelling to the calciner which operates at higher temperatures in the order of 625-800°C. At the temperatures used in this configuration, a 20-38% reduction in the operating temperature is still obtained when compared to thermal oxidizers or any other conventional drainage gas combustion process.

The SDL process is a form of the conventional calcium looping (CCL) process¹⁹⁻²⁴ currently being developed for cleaner power generation via the post combustion capture of CO_2 ⁸. In the CCL process, lime (CaO) is introduced directly to a flue gas stream from a thermal power plant in which CO_2 concentrations can be as high as 12-15%. In comparison, the SDL process introduces CaO to a VAM stream with CH_4 concentrations of 0.1 to 1 vol. % and inert CO_2 concentrations of 0.3 to 2 vol. %. A simplified process flow diagram for the SDL process is depicted schematically in Figure 1. The process can be explained by the looping reactions which occur in the separate calciner and carbonator reactors (See Figure 1). In the calciner reactor, the calcination reaction (R1) is endothermic in which stone dust (CaCO_3) is thermally decomposed in the presence of goaf gas (for no CO_2 capture)/ natural gas and oxidant mixture (for CO_2 capture) at temperatures of 625 - 800 °C while maintaining appropriate CO_2 partial pressure in the calcination reactor, to produce calcium oxide (CaO). After decomposition of stone dust, the CaO formed is then transported to the carbonator reactor where it is exposed to a pre-heated VAM stream. In the carbonator, two strongly exothermic reactions occur simultaneously; the catalytic oxidation of methane (R2) at relatively low temperatures (450-600°C), in comparison to conventional thermal oxidisers, and atmospheric pressure, followed by the capture of CO_2 (R3) produced by the aforementioned reaction via the carbonation of CaO to CaCO_3 . As reactions (R1) and (R3) are redox reactions, by running the calciner in auto-thermal mode an energy vector will be formed between carbonator and calciner. Under this scenario, as illustrated in Figure 1 there is also potential for combined (VAM and goaf gas) power generation by integrating a common steam cycle into the carbonator reactor. More details about the SDL process integration can be found elsewhere⁸.

Calciner Reaction

Carbonator Reactions

Figure 1. Simplified SDL process flow diagram for VAM abatement with optional power generation.

Currently in literature, the focus of studies is the utilisation of fluidised bed carbonators (i.e. the CCL process) to capture CO₂ in flue gas streams from power plants²⁵⁻²⁹, while there is no explicit work on the performance of a fluidized bed carbonator or CCL process in the presence of VAM. The present study aims to derive an empirical model for a continuous SDL process derived from a series of single fluidised bed experiments and implementing the random pore model (RPM) to provide a quantitative understanding of a number of critical operational parameters such as stone dust inventory requirement, stone dust makeup requirement, CaO flux requirements between the carbonator and calciner and reactor footprint. Future studies will build on this study for scale up reactor design which will need to take into consideration both hydrodynamic scaling rules, in conjunction with chemical reaction scaling rule, i.e. selectivity, heat transfer, mass transfer and kinetics.

2. Empirical Model Development

Mathematical modelling of the carbonator in a continuous SDL process allows for the simulation of various conditions under which the carbonator will operate. However, a mathematical model requires experimental data obtained under different operating conditions for model validation and determination of optimum operating conditions. In the absence of a dual fluidised bed experimental setup, it was proposed to perform a series of single fluidised bed reactor experiments to derive the inherent kinetics of the reactions occurring in the carbonator reactor. The primary differences between a single and a dual fluidised bed reactor are that in a single fluidised bed carbonator reactor: (1) the particle feed rate can't be controlled, (2) there is no opportunity for online particle sampling and (3) only a single cycle of pre-calcined sorbent particle occurs. Hence the empirical model developed allows prediction of these unknown parameters in a continuous system utilising the inherent kinetic parameters derived from single fluidised bed experiments.

To determine the inherent kinetic parameters, a series of fluidised bed experiments were performed to derive reaction kinetics for the catalytic oxidation of methane as well as carbonation of methane in the carbonator reactor. The setup utilised in this study was assumed to behave as a plug flow reactor. The assumption of a simplified plug-flow was made considering that a uniform bubble size was used (16-40 μm), the turbulent nature of the flow during bubbling fluidised bed operation, the long length of the reactor and the relatively slow rate of the catalytic oxidation and carbonation reactions. Determination of the apparent kinetic rates given that CaCO_3 will be present i.e. the CO_2 capture reaction will occur simultaneously in the reactor together with the catalytic oxidation of methane, was then completed using the data obtained from experiments that simulated real plant operating conditions. This reaction rate data was then input into the proposed model in order to gain a qualitative understanding of the solids circulation rate, make up flow and inventory requirement for the SDL process. It should be noted that the current exercise is to obtain qualitative information about the solid circulation rate, makeup flow and inventory requirement and not for reactor design. Further details of the experimental and modelling methodologies are described in the following sections.

2.1. Experimental methods

A series of experiments were performed in a single lab scale fluidised bed reactor, shown in Figure 2, at three temperatures (500, 550 and 600 °C), two flow rates of 1% CH₄ in air (250 and 500 mL/min) and three inventory sizes (8, 12 and 16 g) as detailed in the experimental matrix presented in Table 1. The data obtained from these experiments were used to derive kinetic parameters for the catalytic and carbonation reactions to be used in the continuous SDL process model.

Figure 2. Lab scale fluidised bed reactor experimental set up.

Table 1. Experimental matrix of fluidised bed experiments

Case	T (°C)	Mixture Flowrate (mL/min)	Inventory (g)
A	500	250	8
	550		
	600		
B	500	500	8
	550		
	600		
C	500	250	12
	550		
	600		
D	500	500	12
	550		
	600		
E	500	250	16
	550		
	600		
F	500	500	16
	550		
	600		

The experimental setup was comprised of a fluidized bed reactor, furnace, condenser, gas control unit and gas analyser. The reactor was a cylindrical fused-quartz tube (Monash Scientific Ltd.) with a height of 450 mm and diameter of 25 mm. A frit (distributor plate) of porosity 3 (16-40 μm) was placed 280 mm from the bottom of the reactor to ensure that the feed gas was pre-heated before entering the fluidized bed. The reactor temperature was maintained during the experiment by the furnace controller and measured using a Pt/Rh thermocouple. Stone dust material (Omya limestone) was sieved to the preferred particle size of 150-212 μm and kept in an oven at 100 $^{\circ}\text{C}$ prior to experimentation. XRF analysis of the fresh Omya limestone is provided in Table 2. The stone dust was calcined at 850 $^{\circ}\text{C}$ for 3 hours to produce fresh calcined lime (CaO) for use in all calcination experiments. Each experimental condition (as presented in Table 1) was performed three times to ensure repeatability of results.

Table 2: XRF Analysis of stone dust

Ca	Fe	Mg	Al	Si	Mn	K
97.56	0.23	0.38	0.15	1.21	0.43	0.04

2.1.1. Catalytic reaction kinetics

The experimental data obtained from the range of experiments conducted as detailed in Table 1 were used to determine the catalytic reaction rate constant using Equation (1), which can be used to determine the inventory requirement to achieve conversion of methane³⁰.

$$r = k(1 - X_{CH_4})^i \quad (1)$$

where r is the rate of reaction, k is the catalytic reaction kinetic constant defined by the Arrhenius equation, $k = A \exp(-E/RT)$, X_{CH_4} is the fraction of methane consumed and i is the reaction order. Assuming a first order reaction i.e. $i = 1$:

$$Q \frac{dx}{dV} = k(1 - X_{CH_4}) \quad (2)$$

where Q is the feed rate of methane in cubic centimeters per second at STP and V is the bulk volume of catalyst. Finally integration of Equation (2) gives:

$$k = -(Q/V) \ln(1 - X_{CH_4}) \quad (3)$$

Arrhenius plots of $\ln k$ from Equation (3) versus $1000/T$ were then used to determine the activation energy, E , and pre-exponential factor, A , for each of the experimental conditions detailed in Table 1. The kinetic parameters for the catalysts CuO, and Fe_2O_3 were also determined, from a series of experiments previously performed by Shah et al.⁸ An example of the Arrhenius plots obtained for each of the different catalysts is presented in Figure 3 for Case C (Table 1).

Figure 3. Catalytic reaction kinetics Arrhenius plot for Case C.

From the stone dust experimental data obtained for each case presented in Table 1, a mean activation energy, E , of 132.45 kJ/mol and pre-exponential factor, A , of $5.83 \times 10^7 \text{ s}^{-1}$ were obtained for the catalytic oxidation of methane, by plotting a master curve of the data obtained from each experimental case. The same procedure was performed for the other catalysts and the kinetic parameters for each different catalyst are presented in Table 3. It can be seen that CaO reaction kinetics are slower than CuO but faster kinetics than Fe_2O_3 .

Table 3: Comparison of stone dust kinetic parameters with copper and iron catalysts.

Catalyst	$k \times 10^{-2} \text{ (s}^{-1}\text{)}$	$A \times 10^7 \text{ (s}^{-1}\text{)}$	$E \text{ (kJ/mol)}$
CuO	5.17	0.098	96.61
CaO	1.6	5.83	132.45
Fe ₂ O ₃	0.39	6.35	141.16

2.1.2. Carbonation reaction kinetics

In order to derive the activation energy (E_{aK}) and pre-exponential factor (k_{s0}) for the carbonation reaction kinetics, the RPM was used. This model was previously developed and applied for other gas-solid reactions^{31-34,35}. Frequently, un-reacted shrinking core models or grain models are used for gas-solid reactions of non-porous and porous solid reactants, respectively. However, pore models describe the carbonation reaction with a higher precision as they account for the evolution of pore size distribution during cycling³⁶. Modification of a pore model to a grain model, with an appropriate modification to structural parameters, was established by Bhatia and Perlmutter³¹, with good agreement between a grain model and their RPM^{31, 32}. The RPM deliberates the pore structure as a network of randomly interconnected pores, expresses the particle structural parameters based on this geometry and to end with, when it is applied to the carbonation reaction, delivers kinetic parameters by fitting experimental reaction rate data obtained from ‘fresh lime’³⁴.

According to the RPM, the reaction rate of a gas-solid reaction in the presence of a product layer diffusion resistance is expressed by Equation (4)³⁴.

$$\frac{dX}{dt_{reactor}} = \frac{k_s S_0 (C_{CO_2} - C_{e,CO_2})(1-X)\sqrt{1-\psi \ln(1-X)}}{(1-\varepsilon_0) \left[1 + \frac{\beta Z}{\psi} (\sqrt{1-\psi \ln(1-X)} - 1) \right]} \quad (4)$$

where k_s is the rate constant for the surface reaction, S_0 is the reaction surface area per unit of volume, ε_0 is the porosity of the particle, C_{CO_2} is the concentration of CO₂ in the gas bulk, C_{e,CO_2} is the equilibrium concentration of CO₂ at reaction conditions³⁷, X is solids conversion at the exit of the carbonator, ψ relates the internal pore structure of the particle as defined in Equation (5), β is defined in Equation (6) and Z is defined in Equation (7):

$$\psi = \frac{4\pi L_0(1-\varepsilon_0)}{S_0^2} \quad (5)$$

where L_0 represents the initial pore length per unit of volume and S_0 , L_0 and ε_0 can be directly calculated from mercury porosimetry data³³ applied to fresh calcines.

$$\beta = \frac{2k_s \rho_{CaO}(1-\varepsilon_0)}{PM_{CaO} D_p S_{ave}} \quad (6)$$

where ρ_{CaO} is the density of CaO, PM_{CaO} is the molecular weight of CaO, D_p is the apparent product layer diffusion and S_{ave} is maximum average reaction surface.

$$Z = 1 + \frac{\rho_{CaO}(v_{CaCO_3} - v_{CaO})}{PM_{CaO}} \quad (7)$$

where v_{CaCO_3} is the molar volume of $CaCO_3$ and v_{CaO} is the molar volume of CaO.

In Equations (4) – (7), the structural parameters required are detailed in Table 4 for Katowice limestone as obtained from Grasa et al.³⁶ and applied in our model. Katowice limestone properties were used, as their properties are near identical to the Omya limestone used in our experiments. Moreover, they were obtained from experiments performed in the presence of similar reaction conditions.

Table 4. Structural parameters of calcined fresh Katowice limestone input to carbonator model from obtained from literature data³⁶.

Parameter	Value
S_0 (m ² /m ³)	35×10^3
L_0 (m/m ³)	2.63×10^{14}
ε_0 (-)	0.46
ψ (-)	1.41

The reaction rate constant (k_s) was derived by simplifying and integrating terms in Equation (4) which control the regime of the chemical reaction and assuming a first order reversible reaction to give:

$$f(\psi) = \frac{1}{\psi} [\sqrt{1 - \psi \ln(1 - X)} - 1] = \frac{k_s S_0 (C_{CO_2} - C_{e,CO_2}) t}{2(1 - \varepsilon_0)} \quad (8)$$

In the fast reaction regime, the reaction rate constant, k_s , can then be estimated by plotting the left side of Equation (8), $f(\psi)$, against time. Alternatively, k_s , can also be represented by the Arrhenius equation:

$$k_s = k_{s0} \exp(-E_{aK}/RT) \quad (9)$$

Arrhenius plots of $\ln k_s$, where k_s was determined from Equation (8), versus $1000/T$ were then used to determine the activation energy, E_{aK} , and pre-exponential factor, k_{s0} , for each of the experimental conditions detailed in Table 1. An example of the Arrhenius plots obtained is presented in Figure 3 for Case C (Table 1).

Figure 4. Carbonation reaction kinetics Arrhenius plot for Case C.

From the experimental data obtained for each case presented in Table 1, the mean activation energy, E_{aK} , of 23.17×10^3 kJ/kmol and pre-exponential factor, k_{s0} , of 9.81×10^{-6} m⁴/kmol.s were obtained by plotting a master curve of the data obtained from each experimental case. These values are in close agreement with the values reported by Grasa et al.³⁶: E_{aK} of 19.2×10^3 kJ/kmol and k_{s0} of 5.29×10^{-6} m⁴/kmol.s for Katowice limestone, as well as with Sun et al.³⁸: E_{aK} of $29 \pm 4 \times 10^3$ kJ/kmol for Strassburg limestone³⁸.

2.2. Modelling a continuous SDL Process

Utilising the kinetic data obtained from single fluidised bed experiments, a model was developed for a continuous SDL process based on the Random Pore Model (RPM) model for a circulating fluidized-bed reactor³⁴. In this model, the performance of the carbonator is defined by E_{carb} , which is the fraction of CO₂ captured by the calcined limestone particles. The simulation was based on the following assumptions:

- (1) temperature in the carbonator is uniform,
- (2) CO₂ capture efficiency is determined by change in methane conversion with bed inventory constant, meaning there is no change in particle feed rate,

- (3) CO₂ capture efficiency is determined primarily by solid circulation rate (F_{CaO}) and stone dust make-up flow (F_{CaCO_3}),
- (4) complete decomposition of CaCO₃ occurs during calcination.

Figure 5. Mass balance of a continuous stone dust looping process.

A mass balance of the overall continuous SDL process, presented in Figure 5, was performed and can be expressed as ^{39,40}:

$$(\text{CO}_2 \text{ reacting with CaO in the bed}) = (\text{CO}_2 \text{ removed from the gas phase}) = (\text{CaCO}_3 \text{ formed in the circulating stream of CaO}) \quad (10)$$

where each term in Equation (10) can be written as:

$$(\text{CO}_2 \text{ removed from the gas phase}) = F_{CH_4} \times X_{CH_4} \times E_{carb} = F_{CO_{2,in}} \times E_{carb} \quad (11)$$

$$(\text{CaCO}_3 \text{ formed in the circulating stream of CaO}) = F_{CaO} \times X \quad (12)$$

$$(\text{CO}_2 \text{ reacting with CaO in the bed}) = N_{CaO} \times f_a \times r_{ave} \quad (13)$$

where F_{CH_4} is the flow of methane entering the carbonator, X_{CH_4} is methane conversion which is calculated from Equation (3), F_{CaO} is the flow of CaO entering the calciner, X is the solid conversion at the exit of the carbonator, N_{CaO} is number of moles of CaO in the carbonator

including CaO and CaCO₃, f_a is volumetric fraction of CaO reacting in the carbonator in the fast reaction regime and r_{ave} is the average reaction rate of the active material. As previously mentioned, an estimate of CO₂ capture efficiency in the carbonator was defined as E_{carb} , which can be expressed as the ratio of CO₂ reacting with CaO in the bed to CO₂ generated in the bed after catalytic oxidation of methane, which can be written as:

$$E_{carb} = 1 - \frac{F_{CO_2,out}}{F_{CH_4}X_{CH_4}} = 1 - \frac{F_{CO_2,out}}{F_{CO_2,in}} \quad (14)$$

where $F_{CO_2,out}$ is the molar flowrate of CO₂ exiting the carbonator.

In the SDL process, behaviour of the limestone sorbent is a key parameter under repeated cycling as it is known, with an increasing number of cycles there is a decrease in the activity the limestone particles. The average activity depends on the degree of carbonation and calcination of the sorbent and in a continuous process, the rate at which fresh sorbent is added to replace some of the recirculating sorbent. Equation (15) as proposed Rodriguez et al⁴¹ has been adopted to estimate the average activity of the material circulating between the reactors in the model. This is because it links the average activity of sorbent performance parameter with solid circulation flows.

$$X_{ave} = (F_{CaCO_3} + F_{CaO}r_0)f_{calc} \left[\frac{a_1f_1^2}{F_{CaCO_3} + F_{CaO}f_{carb}f_{calc}(1-f_1)} + \frac{a_2f_2^2}{F_{CaCO_3} + F_{CaO}f_{carb}f_{calc}(1-f_2)} + \frac{b}{F_{CaCO_3}} \right] \quad (15)$$

where F_{CaCO_3} represents the make-up flow of fresh limestone, $a_1 = 0.1045$, $f_1 = 0.9822$, $a_2 = 0.7786$, $f_2 = 0.7905$ and $b = 0.07709$ are all sorbent fitting constants as proposed by Zhen-shan et al.⁴² and f_{carb} and f_{calc} are reactor performance indicators defined where f_{calc} is the fraction of calcination of all particles in the system and f_{carb} is the fraction of carbonation of all particles in the system. In Equation (15), X_{ave} represents the maximum amount of conversion of CaO to CaCO₃ in the carbonator. The actual conversions in the carbonator (X_{carb}) and calciner (X_{calc}) can be calculated using Equations (16)⁴¹ and (17)⁴¹, respectively. Note that for this model $f_{calc} = 1$.

$$X_{carb} = \frac{f_{carb}}{1 - (1 - f_{carb})(1 - f_{calc})} X_{ave} \quad (16)$$

$$X_{calc} = (1 - f_{calc})X_{carb} \quad (17)$$

The conversion of the particles is a function of the residence time distribution and assuming that the solids are perfectly mixed, it is possible to calculate the average reaction rate of the CaO particles in the bed, r_{ave} . This was completed by modifying the RPM equation presented in Equation (4) and taking into account the average values of the continuous process as follows:

$$r_{ave} = \frac{k_s S_{ave} (\overline{C_{CO_2}} - C_{e,CO_2}) (1 - X_{ave}) \sqrt{1 - \psi \ln(1 - X_{ave})}}{(1 - \varepsilon_0) \left[1 + \frac{\beta Z}{\psi} (\sqrt{1 - \psi \ln(1 - X_{ave})} - 1) \right]} \quad (18)$$

where S_{ave} is the average reaction surface available for CaO particles entering the carbonator as determined by Equation (20). Equation (20) was formulated as it has been shown that for most types of limestone and irrespective of number of cycles, the maximum conversion of particles is reached at a product layer thickness of 50 nm (e_{max})⁴³. The expression that relates maximum conversion (X_N) with the particle surface reaction early in the cycle (S_N) can be written as:

$$X_N = \frac{e_{max} S_N \frac{\rho_{CaCO_3}}{PM_{CaCO_3}}}{\frac{\rho_{CaO}}{PM_{CaO}}} \quad (19)$$

Hence for S_{ave} , the average reaction surface of the CaO particles is calculated as:

$$S_{ave} = \frac{X_{ave} \frac{\rho_{CaO}}{PM_{CaO}}}{\frac{\rho_{CaCO_3}}{PM_{CaCO_3}}} \quad (20)$$

where PM and ρ are the average molecular weight and density respectively.

Now, the particle structural parameter, ψ , originally presented in Equation (5) can be calculated as a function of average reaction surface, S_{ave} and the average pore length, L_{ave} :

$$\psi = \frac{4\pi L_{ave} (1 - \varepsilon_0)}{S_{ave}^2} \quad (21)$$

where L_{ave} is defined as:

$$L_{ave} = L_0 X_{ave} \quad (22)$$

The average concentration of CO₂ in the carbonator, $(\overline{C_{CO_2}} - C_{e,CO_2})$, was calculated by taking a similar approach as the mean logarithmic by considering the gaseous phase volume for the reaction in the carbonator and can be expressed as:

$$(\overline{C_{CO_2}} - C_{e,CO_2}) = \frac{\rho_{M,g} E_{carb}}{\left[\frac{-f_0}{(f_0 f_e - f_0)} E_{carb} + \frac{f_0(f_0 - 1)}{(f_0 f_e - f_0)^2} \ln \left(\frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(f_0 - f_e)} \right) \right]} \quad (23)$$

where $\rho_{M,g}$ is the molar density of the gas, E_{carb} is the CO₂ capture efficiency, f_0 is the molar fraction of CO₂ which is X_{CH_4} and f_e is the equilibrium molar fraction of CO₂ as calculated using Equation (24)³⁵:

$$f_e = \frac{10^{(7.079 - 8308/T)}}{P_{total}} \quad (24)$$

where T is the operation temperature and P_{total} is the total system pressure.

As already mentioned, the maximum average rate of reaction of the CaO particles is the rate at which the active CaO particles react in the carbonator and therefore, have not reached maximum conversion. The fraction of active particles, f_a , can be defined as the particles that have been unable to react with CO₂ in the carbonator for a sufficient time, t^* , to reach their maximum carbonation conversion³⁹. Hence for a perfectly mixed model, f_a can be expressed as:

$$f_a = \left(1 - e^{-t^*/\tau} \right) \quad (25)$$

where τ is the average particle residence time in the carbonator which is defined as:

$$\tau = \frac{N_{CaO}}{F_{CaO}} = \frac{W_{CaO}}{PM_{CaO} F_{CaO}} \quad (26)$$

where F_{CaO} is the calcium looping rate between the reactors and t^* , the characteristic time at which the reaction rate becomes zero can be calculated from Equation (27):

$$t^* = \frac{X_{ave}}{dX/dt_{reactor}} \quad (27)$$

The conversion of CaO particles in the system obtained is different as a function of residence time, hence Equation (12) was modified as follows:

(CaCO₃ formed in the circulating stream of CaO) =

$$F_{CaO} X = F_{CaO} (f_a X |_{<t^*} + (1 - f_a) X |_{>t^*}) \quad (28)$$

where:

$$X |_{>t^*} = X_{ave} \quad (29)$$

Since r_{ave} is constant between 0 and t^* , $X |_{<t^*}$ can be calculates as follows³⁹:

$$X|_{<t^*} = \frac{\int (r_{ave}t) df_a}{f_a} = \frac{\int_0^{t^*} (r_{ave}t) \frac{1}{\tau} e^{-t/\tau} dt}{f_a} = r_{ave} \tau \frac{[1 - e^{-t^*/\tau} (\frac{t^*}{\tau} + 1)]}{(1 - e^{-t^*/\tau})} \quad (30)$$

Now making Equation (30) a function of f_a gives:

$$X|_{<t^*} = r_{ave} \tau \frac{[1 - (1 - f_a) (\ln(\frac{1}{1 - f_a}) + 1)]}{f_a} \quad (31)$$

Considering all the previous information, the carbon mass balance in the solids phase can be expressed as³⁹:

$$E_{carb} = \frac{F_{CaO}}{F_{CH_4} X_{CH_4}} X_{ave} \frac{f_a}{\ln(1/(1 - f_a))} \quad (32)$$

where F_{CH_4} is the molar flow rate of CH_4 that enters the carbonator.

The carbon mass balance in the gas phase was then formulated based on the knowledge of the rate of reaction of the active particles in the bed³⁹:

$$F_{CH_4} X_{CH_4} \frac{dE_{carb}}{dz} = A f_a \frac{\rho_{CaO}}{PM_{CaO}} r_{ave} = A \cdot f_a \cdot \frac{\rho_{CaO}}{PM_{CaO}} \cdot k_s \cdot S_{ave} \cdot \rho_{M,g} \left[\frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(1 - f_0 E_{carb})} \right] \quad (33)$$

where A is the cross sectional area of the carbonator. The integrated form of Equation (33) in dimensionless form becomes:

$$\frac{F_{CH_4} \cdot X_{CH_4} \cdot PM_{CaO}}{W_{CaO} \cdot k_s \cdot S_{ave} \cdot \rho_{M,g} \cdot f_a \cdot \gamma} \left[\frac{-f_0}{(f_0 f_e - f_0)} E_{carb} + \frac{f_0(f_0 - 1)}{(f_0 f_e - f_0)^2} \ln \left(\frac{(f_0 - f_e) + (f_0 f_e - f_0) E_{carb}}{(f_0 - f_e)} \right) \right] = H' \quad (34)$$

where,

$$\gamma = \frac{(1 - X_{ave}) \sqrt{1 - \psi \ln(1 - X_{ave})}}{(1 - \varepsilon_0) \left[1 + \frac{\beta Z}{\psi} (\sqrt{1 - \psi \ln(1 - X_{ave})} - 1) \right]} \quad (35)$$

Given the system of equations previously defined, the solution to the model was calculated by defining a number of input variables and implementing a MATLAB code that was developed to solve the mass balance of the continuous SDL process. The input variables to be defined were the composition of the gas used in the carbonator and the calciner, the inlet gas velocity in the carbonator and its total inventory, the kinetic and sorbent decay constants, the total solids circulation rate between reactors and the make-up flow of limestone. The MATLAB code developed then applied an iterative procedure to solve the implicit Equation (34) until a solution of f_a yielded carbonation efficiencies in the gas and solid material balances. This was done by:

1) Assuming a value of f_a and calculating the carbonation efficiency, E_{carb} , in two ways:

- i. at the carbonator exit i.e. $H' = 1$ ($E_{carb,1}$)
- ii. by matching the expressions and balancing Equations (32) and (34) to give:

$$E_{carb,2} = \frac{F_{CaO}(f_a X|_{<t^*} + (1-f_a)X|_{>t^*})}{F_{CH_4}} \quad (36)$$

2) The absolute value of the difference of the two E_{carb} values was obtained from the two previous forms, such that:

- If $(E_{carb,1} - E_{carb,2}) > 0.01$, step 1 in this process was repeated and new value of f_a was assumed
- If $(E_{carb,1} - E_{carb,2}) \leq 0.01$, the model is considered solved.

From the continuous SDL process model developed, the fraction of active particles, their maximum CO₂ carrying capacity and carbonation conversion, the calcium looping rate between reactors and CO₂ capture efficiency in the carbonator can all be calculated. Results of the model application for a typical 1 m³/s VAM flow rate with 1 vol% CH₄ concentration are presented in the following section.

3. Results and Discussion

Three critical parameters were identified for investigation using the continuous SDL process model developed; the calcium looping ratio, the makeup ratio and the inventory size. The calcium looping ratio was defined as the ratio of the molar flowrate of CaO entering the carbonator to the molar flowrate of CH₄ entering the carbonator (F_{CaO}/F_{CH_4}), the makeup ratio was defined as the molar flowrate of fresh limestone entering the calciner to the molar flowrate of CH₄ entering the carbonator (F_{CaCO_3}/F_{CH_4}) and the inventory size was represented by W_{CaCO_3} . The effect of these critical parameters on the CO₂ capture efficiency in the carbonator (E_{carb}), the conversion of methane to CO₂ in the carbonator (X_{CH_4}) and the ultimate feasibility of the SDL process are presented.

3.1. Effect of calcium looping ratio (F_{CaO}/F_{CH_4})

Figure 6 presents the effect of calcium looping ratio on the equilibrium-normalized CO₂ capture efficiency (E_{carb}/E_{eq}) and sorbent CaO conversion (X_{carb}) for a carbonator temperature of 500°C, makeup ratio of 0.1, inventory size of 30,000 kg and methane conversion of 98%. A methane conversion of 98% was chosen considering that during practical operation, due to

economic and operational constraints, 100% methane conversion is rarely achievable, while a maximum conversion of 98% is more likely. Only the solids circulation rate, i.e. F_{CaO} , was varied while the methane flow was kept constant. It was observed that an increase in the calcium looping ratio, from 1 to 5, resulted in a lower carbonated bed fraction, from 0.35 to around 0.18, at the same time this led to an increase in CO₂ capture efficiency in the carbonator, from 0.35 to almost 1. This can be explained by the increase in the F_{CaO}/F_{CH_4} ratio which ultimately led to an increase in the carbonation rate of the whole carbonator inventory (N_{CaO}), due to the increase in active sites in the inventory.

Figure 6. Calcium looping ratio (F_{CaO}/F_{CH_4}) vs. equilibrium-normalized CO₂ capture efficiency (E_{carb}/E_{eq}) and sorbent CaO conversion (X_{carb})

3.2. Effect of make-up ratio (F_{CaCO_3}/F_{CH_4})

Figure 7 presents the CO₂ capture efficiency (E_{carb}) as a function of different make up ratios (F_{CaCO_3}/F_{CH_4}) and solids circulation ratios (F_{CaO}/F_{CH_4}) at a typical CH₄ conversion of 98%. It was observed that increasing the makeup ratio, i.e. F_{CaCO_3}/F_{CH_4} , directly resulted in an increase in CO₂ capture efficiency as did increasing the solids circulation rate, i.e. F_{CaO}/F_{CH_4} . It can also be seen that to achieve the equilibrium capture efficiency ($E_{carb,eq}$) at each temperature, different inventory sizes and make-up ratios were required. For an F_{CaO}/F_{CH_4} ratio of 5, at 600°C the solid inventory requirement was 3 tonnes and an F_{CaCO_3}/F_{CH_4} ratio of ~0.06, whereas for 450°C, 110 tonnes of inventory and an F_{CaCO_3}/F_{CH_4} ratio of ~0.15 were required. Based on the modelling results in Figure 7, to achieve high CO₂ capture efficiencies for 1 m³/s of VAM with 1 vol. % methane, a much smaller range of solid circulation rates are required when there is a make-up

flow of fresh limestone that improves the average activity or carbonation capacity of the material circulating between the reactors.

Figure 7. Carbonation efficiency as a function of make-up ratio at a different solid circulation ratios, temperatures and solid inventories

3.3. Effect of bed inventory size (W_{CaCO_3})

The effect of bed inventory size in the carbonator is presented in Figure 8 for four different carbonator temperatures (i.e. 450, 500, 550 and 600°C). It was observed that at lower temperatures, a higher bed inventory was required to achieve equilibrium capture efficiency. However, with increasing bed inventory size at all temperatures, CO₂ capture efficiency

declined. This was considered an effect of the higher conversion of CH_4 . In order to maintain high CO_2 capture efficiencies in the carbonator the $F_{\text{CaO}}/F_{\text{CH}_4}$ ratio must be increased. The results show that to achieve equilibrium capture efficiency at 600°C , a low $F_{\text{CaO}}/F_{\text{CH}_4}$ ratio of 2 is required, whereas at 450°C , a $F_{\text{CaO}}/F_{\text{CH}_4}$ ratio greater than 2 is required.

Figure 8. Solid inventories (W_{CaCO_3}) vs. Carbonation efficiency (E_{carb}) and methane conversion (X_{CH_4}) at different temperature

3.4. Feasibility of SDL Process

Based on the modelling results for the carbonator, a number of basic feasibility gauges were derived for the SDL Process. The reactor footprint needed to treat a VAM flowrate of $100 \text{ m}^3/\text{s}$ at different reactor temperatures was estimated using the CLFBSPACE model⁵ being developed at the University of Newcastle and is presented in Figure 9. It can be seen as the

carbonator operating temperature increases the reactor footprint significantly decreases. This decrease is due to the lesser amount of bed inventory required and greater CH₄ conversion at higher carbonator operating temperatures, due to relatively faster kinetics and lesser CO₂ capture. For comparison, the footprint of the commercially available MEGTEC Vocsidiser²⁴ is also presented in Figure 9. The SDL Process compares favourably both in terms of overall footprint and operating temperature.

Figure 9. SDL process footprint to treat 100 m³/s of VAM as a function of reactor operating temperature, with the required footprint for the MEGTEC Vocsidiser to treat 70 m³/s of VAM²⁴ for comparison.

The total annual costs of the makeup limestone requirement of the SDL process was also calculated as presented in Table 5 assuming a limestone cost of \$350 AUD per tonne.

Table 5. Requirement and cost of makeup limestone for an SDL process treating 100 m³/s of VAM.

Details	Makeup Ratio (F_{CaCO_3}/F_{CH_4})		
	0.05	0.10	0.15
Make up requirement (tonne/year)	1,920	3,855	5,775
Make up Cost (\$AUD/year)	672,000	1,349,376	2,021,376

It can be seen for a makeup ratio of 0.1, the total annual limestone costs would be approximately \$ 1.35 million AUD. This in comparison to the revenue generation through electricity production would be negligible in the order of 10-30% of total costs⁴⁴.

4. Conclusions

An empirical model was constructed to answer several unknowns of the continuous SDL process such as stone dust inventory requirement, stone dust makeup requirement, CaO flux requirements between the carbonator and calciner and reactor footprints. From the results obtained from the empirical model it was concluded that:

- (1) Increasing the solid circulation rate improved the CO₂ capture efficiency of the carbonator under a constant CO₂ concentration, when make-up flow of fresh limestone was increased.
- (2) Increasing the solids inventory, increased the CH₄ conversion and reduced the CO₂ capture efficiency of the carbonator at different F_{CaO}/F_{CH_4} and F_{CaCO_3}/F_{CH_4} ratios.
- (3) Operationally, the CO₂ capture efficiency was found to increase with increasing calcium looping ratio, attributed to the increase in the fraction of free active CaO in the carbonator bed, increasing the carbonation reaction rate and leading to an increase in CO₂ capture efficiency.
- (4) The inventory requirement in the SDL process is higher than a CCL process if higher capture efficiencies are to be achieved.
- (5) The operating cost of make-up limestone flow is estimated to be 10-30% of the total operating costs of an SDL process.
- (6) The reactor footprint of the SDL process at 600°C is comparable to conventional commercially available thermal oxidiser technology.

5. Nomenclature

F_{CH_4} =CH₄ molar flow rate at the inlet of the carbonator, kmol/s

D_p = apparent product layer diffusion

E_{carb} =CO₂ capture efficiency in the carbonator

X_{CH_4} =Conversion of methane to CO₂

F_{CO_2} = CO₂ molar flow rate reacting with CaO in the bed, kmol/s

F_{CaO} =molar flow rate of CaO coming from the calciner, kmol/s

W_{CaO} =solid inventory in the carbonator, kg

N_{Ca} =mol of Ca in the carbonator including CaO and CaCO₃, kmol

f_a =volumetric fraction of CaO at that reacts in the carbonator in the fast reaction regime

r_{ave} =average reaction rate of active material, s⁻¹

C_{CO_2} =concentration of CO₂, kmol/m³

C_{e,CO_2} =the CO₂ equilibrium concentration at reaction conditions, kmol/m³

e_{max} =maximum thickness of the layer of CaCO₃ on the pore wall, 50 nm

f_0 =inlet mole fraction of CO₂

f_e =molar fraction of CO₂ at the point of equilibrium in the reaction conditions

f_a =volumetric fraction of CaO that reacts in the carbonator in the fast reaction regime

F_{CaCO_3} =molar flow rate of fresh limestone, kmol/s

k_s =kinetic constant, m⁴/ (kmol s)

k_{s0} = pre-exponential factor in Eq. 11, m⁴/ (kmol s)

N_{CaO} =mol of CaO in the carbonator including CaO and CaCO₃, kmol

S_{ave} =maximum average reaction surface, m⁻¹

S_0 =initial surface area per unit volume

X_{ave} =maximum average conversion of solids

ε_0 =porosity

S_N =reaction surface in the N cycle, m⁻¹

ρ_{CaO} =CaO density, kg/m³

ρ_{CaCO_3} = CaCO₃ density, kg/m³

$\rho_{M,g}$ =molar density of the gas, kmol/m³

PM_{CaCO_3} =molecular weight of CaCO₃, kg/kmol

PM_{CaO} =molecular weight of CaO, kg/kmol

v_{CaCO_3} =molar volume of CaCO₃, m³/kmol

v_{CaO} = molar volume of CaO, m³/kmol

X_N = maximum conversion of particles in the N cycle

N = number of calcination and full carbonation cycles

X = solid conversion at the exit of the carbonator

A = carbonator section, m²

τ = average residence time in the carbonator, s

t^* = characteristic time at which the reaction rate becomes zero, s

$X |_{<t^*}$ = conversion of particles with a residence time lower than t^*

$X |_{>t^*}$ = conversion of particles with a residence time higher than t^*

a, b = stoichiometric coefficient for carbonation reaction

E_{aK} = activation energy for kinetic regime, K, kJ/kmol

Z = ratio volume fraction after and before reaction

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7. References

- (1) Karacan, C. Ö.; Ruiz, F. A.; Cotè, M.; Phipps, S. Coal mine methane: a review of capture and utilization practices with benefits to mining safety and to greenhouse gas reduction. *International Journal of Coal Geology* **2011**, 86 (2), 121-156.
- (2) Karakurt, I.; Aydin, G.; Aydinler, K. Mine ventilation air methane as a sustainable energy source. *Renewable and Sustainable Energy Reviews* **2011**, 15 (2), 1042-1049.

- (3) Carothers, P.; Deo, M., *Technical and economic assessment: Mitigation of methane emissions from coal mine ventilation air*. United States, Environmental Protection Agency, Climate Protection Division: 2000.
- (4) Mallett, C.; Su, S. In Progress in developing ventilation air methane mitigation and utilization technologies, *Third International methane and nitrous oxide mitigation conference, Beijing* 2003.
- (5) Zhou, C.; Shah, K.; Moghtaderi, B. Techno-Economic Assessment of Integrated Chemical Looping Air Separation for Oxy-Fuel Combustion: An Australian Case Study. *Energy & Fuels* **2015**, 29 (4), 2074-2088.
- (6) Zhou, C.; Shah, K.; Doroodchi, E.; Moghtaderi, B. Equilibrium thermodynamic analyses of methanol production via a novel Chemical Looping Carbon Arrestor process. *Energy Conversion and Management* **2015**, 96, 392-402.
- (7) Shah, K.; Zhou, C.; Song, H.; Doroodchi, E.; Moghtaderi, B. A Novel Hybrid Chemical-Looping Oxy Combustor Process for the Combustion of Solid and Gaseous Fuels: Thermodynamic Analysis. *Energy & Fuels* **2015**, 29 (2), 602-617.
- (8) Shah, K.; Moghtaderi, B.; Doroodchi, E.; Sandford, J. A feasibility study on a novel stone dust looping process for abatement of ventilation air methane. *Fuel Processing Technology* **2015**, 140, 285-296.
- (9) Ramezani, M.; Shah, K.; Doroodchi, E.; Moghtaderi, B. Application of a novel calcium looping process for production of heat and carbon dioxide enrichment of greenhouses. *Energy Conversion and Management* **2015**, 103, 129-138.
- (10) Peng, Z.; Doroodchi, E.; Alghamdi, Y. A.; Shah, K.; Luo, C.; Moghtaderi, B. CFD–DEM simulation of solid circulation rate in the cold flow model of chemical looping systems. *Chemical Engineering Research and Design* **2015**, 95, 262-280.
- (11) Alghamdi, Y.; Peng, Z.; Shah, K.; Moghtaderi, B.; Doroodchi, E. Predicting the Solid Circulation Rate in Chemical Looping Combustion Systems Using Pressure Drop Measurements. *Powder Technology* **2015**.
- (12) Song, H.; Shah, K.; Doroodchi, E.; Wall, T.; Moghtaderi, B. Reactivity of Al₂O₃-or SiO₂-Supported Cu-, Mn-, and Co-based oxygen carriers for chemical looping air separation. *Energy & Fuels* **2014**, 28 (2), 1284-1294.
- (13) Song, H.; Shah, K.; Doroodchi, E.; Wall, T.; Moghtaderi, B. Analysis on chemical reaction kinetics of CuO/SiO₂ oxygen carriers for chemical looping air separation. *Energy & Fuels* **2013**, 28 (1), 173-182.
- (14) Song, H.; Shah, K.; Doroodchi, E.; Moghtaderi, B. Development of a Cu–Mg-based oxygen carrier with SiO₂ as a support for chemical looping air separation. *Energy & Fuels* **2013**, 28 (1), 163-172.

- (15) Shah, K.; Moghtaderi, B.; Zanganeh, J.; Wall, T. Integration options for novel chemical looping air separation (ICLAS) process for oxygen production in oxy-fuel coal fired power plants. *Fuel* **2013**, *107*, 356-370.
- (16) Shah, K.; Moghtaderi, B.; Wall, T. Effect of flue gas impurities on the performance of a chemical looping based air separation process for oxy-fuel combustion. *Fuel* **2013**, *103*, 932-942.
- (17) Shah, K.; Moghtaderi, B.; Wall, T. Selection of suitable oxygen carriers for chemical looping air separation: a thermodynamic approach. *Energy & Fuels* **2012**, *26* (4), 2038-2045.
- (18) Moghtaderi, B.; Zanganeh, J.; Shah, K.; Wu, H. Application of concrete and demolition waste as CO₂ sorbent in chemical looping gasification of biomass. *Energy & Fuels* **2012**, *26* (4), 2046-2057.
- (19) Romano, M. C.; Martínez, I.; Murillo, R.; Arstad, B.; Blom, R.; Ozcan, D. C.; Ahn, H.; Brandani, S. Process simulation of Ca-looping processes: review and guidelines. *Energy Procedia* **2013**, *37*, 142-150.
- (20) Abanades, J. C.; Anthony, E. J.; Wang, J.; Oakey, J. E. Fluidized bed combustion systems integrating CO₂ capture with CaO. *Environmental Science & Technology* **2005**, *39* (8), 2861-2866.
- (21) Abanades, J. C.; Grasa, G.; Alonso, M.; Rodriguez, N.; Anthony, E. J.; Romeo, L. M. Cost structure of a postcombustion CO₂ capture system using CaO. *Environmental science & technology* **2007**, *41* (15), 5523-5527.
- (22) Arias, B.; Diego, M.; Abanades, J.; Lorenzo, M.; Diaz, L.; Martínez, D.; Alvarez, J.; Sánchez-Biezma, A. Demonstration of steady state CO₂ capture in a 1.7 MW th calcium looping pilot. *International Journal of Greenhouse Gas Control* **2013**, *18*, 237-245.
- (23) Dieter, H.; Bidwe, A. R.; Varela-Duelli, G.; Charitos, A.; Hawthorne, C.; Scheffknecht, G. Development of the calcium looping CO₂ capture technology from lab to pilot scale at IFK, University of Stuttgart. *Fuel* **2014**, *127*, 23-37.
- (24) MEGTEC Ventilation Air Methane (VAM) Processing MEGTEC Solutions for VAM Abatement, Energy Recovery & Utilization. <http://www.megtec.com/documents/MEGTEC%20VAM%20Processing.pdf>
- (25) Yang, Y.; Zhai, R.; Duan, L.; Kavosh, M.; Patchigolla, K.; Oakey, J. Integration and evaluation of a power plant with a CaO-based CO₂ capture system. *International Journal of Greenhouse Gas Control* **2010**, *4* (4), 603-612.
- (26) Xu, G.; Jin, H.; Yang, Y.; Xu, Y.; Lin, H.; Duan, L. A comprehensive techno-economic analysis method for power generation systems with CO₂ capture. *International journal of energy research* **2010**, *34* (4), 321-332.
- (27) Martínez, I.; Murillo, R.; Grasa, G.; Abanades, J. Integration of a Ca-looping system for CO₂ capture in an existing power plant. *Energy Procedia* **2011**, *4*, 1699-1706.
- (28) Martínez, I.; Murillo, R.; Grasa, G.; Carlos Abanades, J. Integration of a Ca looping system for CO₂ capture in existing power plants. *AIChE Journal* **2011**, *57* (9), 2599-2607.

- (29) Romano, M. C. Modeling the carbonator of a Ca-looping process for CO₂ capture from power plant flue gas. *Chemical Engineering Science* **2012**, 69 (1), 257-269.
- (30) Anderson, R.; Stein, K.; Feenan, J.; Hofer, L. Catalytic oxidation of methane. *Industrial & Engineering Chemistry* **1961**, 53 (10), 809-812.
- (31) Bhatia, S. K.; Perlmutter, D. D. A random pore model for fluid-solid reactions: I. Isothermal, kinetic control. *AIChE Journal* **1980**, 26 (3), 379-386.
- (32) Bhatia, S. K.; Perlmutter, D. D. A random pore model for fluid-solid reactions: II. Diffusion and transport effects. *AIChE Journal* **1981**, 27 (2), 247-254.
- (33) Gavals, G. R. A random capillary model with application to char gasification at chemically controlled rates. *AIChE Journal* **1980**, 26 (4), 577-585.
- (34) Bhatia, S.; Perlmutter, D. Effect of the product layer on the kinetics of the CO₂-lime reaction. *AIChE Journal* **1983**, 29 (1), 79-86.
- (35) Barker, R. The reversibility of the reaction $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$. *Journal of applied Chemistry and biotechnology* **1973**, 23 (10), 733-742.
- (36) Grasa, G.; Murillo, R.; Alonso, M.; Abanades, J. C. Application of the random pore model to the carbonation cyclic reaction. *AIChE journal* **2009**, 55 (5), 1246-1255.
- (37) Baker, E. 87. The calcium oxide–carbon dioxide system in the pressure range 1–300 atmospheres. *Journal of the Chemical Society (Resumed)* **1962**, 464-470.
- (38) Sun, P.; Grace, J. R.; Lim, C. J.; Anthony, E. J. Determination of intrinsic rate constants of the CaO–CO₂ reaction. *Chemical Engineering Science* **2008**, 63 (1), 47-56.
- (39) Alonso, M.; Rodríguez, N.; Grasa, G.; Abanades, J. Modelling of a fluidized bed carbonator reactor to capture CO₂ from a combustion flue gas. *Chemical Engineering Science* **2009**, 64 (5), 883-891.
- (40) Rodríguez, N.; Alonso, M.; Abanades, J. Experimental investigation of a circulating fluidized-bed reactor to capture CO₂ with CaO. *AIChE Journal* **2011**, 57 (5), 1356-1366.
- (41) Rodríguez, N.; Alonso, M.; Abanades, J. Average activity of CaO particles in a calcium looping system. *Chemical Engineering Journal* **2010**, 156 (2), 388-394.
- (42) Zhen-shan, L.; Ning-sheng, C.; Croiset, E. Process analysis of CO₂ capture from flue gas using carbonation/calcination cycles. *AIChE journal* **2008**, 54 (7), 1912-1925.
- (43) Alvarez, D.; Abanades, J. C. Determination of the critical product layer thickness in the reaction of CaO with CO₂. *Industrial & engineering chemistry research* **2005**, 44 (15), 5608-5615.
- (44) Shah, K.; Zhang, Y.; Doroodchi, E.; Moghtaderi, B. In Development of Novel Stone Dust Looping Process for Mitigation of Ventilation Air Methane, *3rd International Conference on Chemical Looping, Chalmers University of Technology; Gothenburg, Sweden. 2014.*