CO2 CAPTURE METHOD USING A COUNTERCURRENT MOVING BED REACTOR

Abstract

This invention discloses a method to capture CO_2 from a gas using Ca-containing porous solids composed of $Ca(OH)_2$ and/or CaO, arranged in a packed bed to contact with the gas. The method is characterized by the use of a carbonator reactor operated in a countercurrent moving bed mode. Such configuration provides the conditions to generate an autothermal central region in the reactor at optimum carbonation temperature between 600-700° C. when using Ca-containing stones, pellets or extruded bricks with effective diameters or thickness between 1-10 cm and solid residence times between 1 to 20 hours, when treating gases with CO_2 content between 2-25% v. In another embodiment, the method provides optimum conditions for efficient CO_2 capture from gases with CO_2 content below 2% v, including ambient air, at temperatures below 100° C. and relative humidity between 80-100%, to achieve maximum carbonation conversion with solid residence times between 20 to 200 hours.

Publication Classification

Int. Cl.: **B01D53/83** (20060101); **B01D53/62** (20060101)

U.S. Cl.:

CPC   **B01D53/83** (20130101); **B01D53/62** (20130101); B01D2251/404 (20130101); B01D2251/602 (20130101); B01D2251/604 (20130101); B01D2253/112 (20130101); B01D2253/1124 (20130101); B01D2253/304 (20130101); B01D2253/306 (20130101); B01D2253/311 (20130101); B01D2257/504 (20130101); B01D2258/0283 (20130101)

Background/Summary

OBJECT OF THE INVENTION

[0001] This invention discloses a method to capture CO_2 from a gas using Ca-containing porous solids composed of $Ca(OH)_2$ and/or CaO, arranged in a packed bed to contact with the gas. The method is characterized by the use of a carbonator reactor operated in a countercurrent moving bed mode. Such configuration provides the conditions to generate an autothermal central region in the reactor at optimum carbonation temperature between 600-700° C. when using Ca-containing stones, or extruded bricks or pellets with effective diameters or thickness between 1-10 cm and solid residence times between 1 to 20 hours, when treating gases with CO_2 content between 2-25% v. In another embodiment, the method provides optimum conditions for efficient CO_2 capture from gases with CO_2 content below 2% v, including ambient air, at temperatures below 100° C. and relative humidity between 80-100%, to achieve maximum carbonation conversion with solid residence times between 20 to 200 hours.

BACKGROUND OF THE INVENTION

[0002] CO_2 capture and permanent storage of CO_2 is a useful climate change mitigation tool to decarbonize fossil-fuel based industries, provide pure CO_2 for industrial uses, or even transform processes into negative emission systems when they are fuelled by biomass, carbon neutral waste or CO_2 directly captured from the atmosphere.

[0003] Calcium Looping, CaL, is a CO_2 capture technology that uses CaO (and/or $Ca(OH)_2$) as regenerable Ca-sorbent of CO_2. The state of the art of the fundamentals properties of the materials, reactor design and process integration of Calcium Looping has greatly progressed in recent years. A wide variety of patents and technical publications have been published to apply Calcium Looping to power plants and industries. For example, U.S. Pat. No. 8,226,917B2 shows that these materials can carbonate fast (in particular $Ca(OH)_2$) when in small particle form (i.e. particle diameter of less than 3 mm), at temperatures between 60° and 700° C. and in a wide range of CO_2 concentrations reach a maximum carbonation conversions of between 0.5-0.7. Such limit to the carbonation conversion is known to be limited by porosity ($CaCO_3$ molecular volume density is 27100 mol/m^3, $Ca(OH)_2$ is 29900 mol/m^3 while CaO is 59642 mol/m^3) and by the formation of a product layer of $CaCO_3$ on the internal surface of CaO. The thickness of the product layer is known to decrease with temperature (Y. A. Criado et al, Effect of the carbonation temperature on the CO_2 carrying capacity of CaO, Ind. Eng. Chem. Res. 2018, 57, 12595-12599). From a practical point of view, this means that for flue gases with CO_2 content between 1-30% v of CO_2 the maximum level of conversion of 0.5-0.7 is reached when the surface area of the Ca-material is higher than 10 m^2/g and the porosity of active Ca-containing material is higher than 0.45.

[0004] Calcium Looping processes making use such Ca-containing materials typically use fluidized

beds, circulating fluidized bed or entrained beds carbonator reactors, where the Ca-sorbents will typically carbonate in seconds to several minutes while in contact with the gas containing CO_2. Once carbonated, the particles containing $CaCO_3$ need to be brought to temperatures typically within 900-950° C. to produce CaO (that eventually returns to the carbonator reactor or is purged for cement manufacture or other uses), and a gas stream rich in CO_2 (suitable for purification and disposal or use).

[0005] There are also Calcium Looping systems using packed bed reactors, where gases can move through the bed but solids do not move and are not carried or entrained by the gas. All known packed bed Calcium Looping systems work in cyclic stages of reaction, with at least one carbonation stage aimed at the generation of a gas with a low content of CO_2 at the exit of the reactor, until the bed of CaO-containing solids is converted to $CaCO_3$ and a sharp breakthrough in the gas composition at the exit of the reactor occurs. For example, U.S. Pat. No. 5,509,362 discloses a fuel gas reforming method with steam, using an adiabatic packed bed reactor filled with CaO sorbent, in which the removal of CO_2 forming $CaCO_3$ shifts the gas reactions towards a higher production of H_2. A subsequent calcination stage of $CaCO_3$ in the same solid bed is carried out using an oxidation/reduction chemical loop and air, so that CO_2 is emitted to the atmosphere in diluted form. US2012/0164032A1 discloses an adiabatic Calcium Looping system to reduce the carbon content in a syngas using a packed-bed reactor holding a calcium-based sorbent.

[0006] Another process to capture CO_2 that uses stagnant solids during carbonation is a system proposed for the direct CO_2 capture from air (Abanades et al., An air CO_2 capture system based on the passive carbonation of large $Ca(OH)_2$ structures, Sust. Energ. & Fuels, 2020, 4, 3409-3417), where the carbonation of porous plates or Ca-containing solids of $Ca(OH)_2$ takes place in the open atmosphere, arranged in vast stationary infrastructures that passively carbonate in weeks to months when left to expose to ambient air. The $Ca(OH)_2$ porous structures can take virtually any form and, once carbonated, can be transported to a centralised calcination plant to manufactured again the $Ca(OH)_2$ while producing pure CO_2. Mortars containing $Ca(OH)_2$ have been extensively used in construction from Roman times, usually mixed up with other materials to enhance mechanical and other properties. The porosity of $Ca(OH)_2$ mortars when settled and dry can be high (between to 0.5-0.7) and this allows almost complete carbonation in ambient air. However, the carbonation mechanism of Ca-containing solids at low temperatures (from ambient air to 100° C.) is known to be different than at 600-700° C. referred above for Calcium Looping applications. Beruto et al (Liquid-like H_2O adsorption layers to catalyze the $Ca(OH)_2/CO_2$ solid-gas reaction and to form a non-protective solid product layer at 20° C. J. Eur. Ceram. Soc. 2000, 20 (4), 497-503) show the need of high relative humidity (80-100%) in the gas to promote fast carbonation of $Ca(OH)_2$. On the other hand, when $Ca(OH)_2$ is flooded in liquid water (for example $Ca(OH)_2$ as "lime putty" used in the building industry), the carbonation rates become again extremely slow. In these conditions, the carbonation rate of $Ca(OH)_2$ dry porous mortars, or other structures containing $Ca(OH)_2$, is governed by CO_2 gas diffusion through the open pores, with a carbonation front moving inwards from the external surface of the porous Ca-containing solids. It must be noted that direct carbonation of CaO at ambient temperatures is so slow that it cannot have practical applications. CaO carbonation in humid air is first converted to $Ca(OH)_2$ by hydration and then form $CaCO_3$.

[0007] An example of an existing industrial application of passive carbonation of $Ca(OH)_2$ to capture CO_2 from air, or vitiated air, comes from the need to remove CO_2 in fruit stores to extend the lifetime of the fruit. A porous bed of $Ca(OH)_2$ in powder form is located inside porous bags for this purpose (FRUITCAL® http://www.carmeuse-agriculture.com/our-products/fruitcal). The bags are simply replaced when fully carbonated. Curing of lime mortars and other cementitious materials containing $Ca(OH)_2$ by the CO_2 contained in air, or

accelerated curing with gases containing CO_2, is also part of the state of the art in the manufacture of extruded bricks or other prefabricated construction structures of a variety of shapes.

[0008] Finally, a recent paper (Lisbona et al. Technoeconomic feasibility study of cement plants as reference facilities for centralized CO_2 capture in industrial sites; 15th International Conference on Greenhouse Gas Control Technologies, GHGT-15, 15-18 Mar. 2021, Abu Dhabi, UAE) proposes the use of centralized cement plants with CO_2 capture (for example by oxycombustion in the calciner fed with $CaCO_3$) as centralized producers of CaO-containing solids, that are then transported (at temperatures close to ambient temperature) to an industrial site to be carbonated in a carbonator reactor operating at around the optimum temperature for Calcium Looping carbonation, i.e. around 650° C. The CaO must be transported at close to ambient temperature and the resulting carbonate requires cooling before being transported for regeneration in the cement plant. Such carbonator is therefore energy and resource inefficient, because it needs arranging additional heat exchanging steps to preheat the CaO-containing solids, the stack flue gases (usually emitted at temperatures below 150° C.) and to recover the energy released in the carbonator or when cooling the carbonated solids exiting the carbonator. Such level of thermal integration may be uneconomic for many industrial applications of relatively small scale, served by the decentralized CO_2 capture carbonation method. A higher level of energy efficiency and compactness would be desirable for such decentralized carbonation method, combined with centralized regeneration to produce CO_2. Indeed, in all applications mentioned above, when the CO_2 sorbent and the resulting carbonate need to be transported at ambient temperature from the regeneration plant to the CO_2 capture plant and vice versa, it would be desirable to have a CO_2 capture method by carbonation being highly energy efficient and economic when preheating and cooling reactants and products from carbonation taking place at optimum temperatures around 650° C. Alternatively, it would be desirable to be able to operate the carbonator at low temperatures, so that transport of sorbent Ca-materials and $CaCO_3$ product would feasible without expensive and energy inefficient heating and cooling steps.

[0009] In this context, it is interest for this invention to note the widespread commercial availability of vertical shaft kilns of limestone to produce porous CaO, with the highest energy efficiencies and lowest footprint. This is achieved in lime kilns by arranging the solids and the gases to move in countercurrent mode in a moving bed apparatus, so that the hot gases leaving the calcination zone (which is overall exothermic because of the firing of a fuel in air to drive the endothermic calcination reaction) preheat the solids entering at ambient temperature at the top of the kiln and the hot solids moving downwards from the calcination zone preheat the air flowing upwards towards the burning zone (H. Piringer, Lime Shaft Kilns, Energy Procedia 120, 2017, 75-95). These moving beds kilns can treat large stones of limestone and lime (from 1 to 15 cm of diameter) to minimise gas pressure drop. They also provide solid residence time of the solids as long as 24 hours, which are needed to achieve the desired calcination degrees of the stones and the effective heat transfer between the gases and the solids in the preheating regions of gases and solids surrounding the calcination zone. In contrast, the gases reside in the kiln less than 20 seconds, moving upwards at superficial gas velocities of 1-3 m/s at the conditions of the calcination zone. The design techniques of cocurrent and countercurrent moving bed reactors are well known, and there are recent moving bed reactors applications in the CO_2 capture field, using special materials and set ups for effective adsorption of CO_2 by the solids (Mondino et al., Moving bed temperature swing adsorption for CO_2 capture from a natural gas combined cycle power plant, International Journal of Greenhouse Gas Control, 85, 2019, 58-70)

[0010] From the previous review of the state of the art, it can be concluded that despite recent advances developing Calcium Looping CO_2 capture methods at high temperatures (using 600-700° C. for carbonation and 900-950° C. for calcination), and the industrial experience related to the producing of porous CaO and $Ca(OH)_2$ materials in stone or Ca-containing solids form, or in the form of porous mortars of $Ca(OH)_2$ of different shapes, or even in the form of porous

bags of Ca(OH).sub.2 material for passive carbonation in contact with air, there is a lack of techno-economically viable and energy efficient CO.sub.2 carbonation methods when the Ca-containing solids entering the carbonator are at low temperature and the exiting carbonated solids must be also at low temperatures (i.e. for transport to a centralized calciner). Decoupling the CO.sub.2 capture step (i.e. by carbonation of low cost sorbent containing Ca(OH).sub.2 and CaO) from the sorbent regeneration stage (i.e. by calcination of CaCO.sub.3 to produce pure CO.sub.2 and regenerate the sorbents) opens up new opportunities for novel CO.sub.2 capture methods. Such methods of capture of CO.sub.2 by carbonation could find a wide range of applications, from flue gases at stack temperatures emitted from industries and freight transport to CO.sub.2 capture from air. This patent discloses such a method of CO.sub.2 capture by carbonation.

DESCRIPTION OF THE INVENTION

[0011] This invention discloses a method to capture CO.sub.2 from a gas entering a thermally insulated packed bed reactor of Ca-containing solids composed of CaO, Ca(OH).sub.2 or mixtures thereof, that can react to form CaCO.sub.3 and obtain a gas depleted in CO.sub.2 at a reactor gas exit; said solids arranged in the form of porous Ca-containing solids, such as lime rocks, extruded bricks or plates made with mortars, or porous bags containing the Ca-containing solids in powder form, to avoid their entrainment into the gas; said solids having, when calcined, internal porosities connected to the exterior surface of the solids ranging between 0.45-0.7 and internal surface areas higher than 10 m.sup.2/g. Such properties allow a maximum molar carbonation conversion of CaO and Ca(OH).sub.2 higher than 0.5, at optimum temperatures of carbonation of 600-700° C. or at ambient temperature as long as there is 80-100% humidity in the air. The method being characterized by: [0012] i. feeding the Ca-containing solids to the gas exit of the reactor at a molar rate of 1-2 times the molar rate of CO.sub.2 contained in the gas; [0013] ii. discharging the CaCO.sub.3-containing solids from a gas inlet of the reactor such that a countercurrent movement of the gas respect to the solids is generated; [0014] iii. providing a residence time to the solids in the reactor between 1-200 hours. As will be revealed by experiments and simulations discussed below, this wide range in residence times is because the method will target gases with a content of CO.sub.2 as high as 25% v to ambient air (with just about 500 ppmv CO.sub.2), that will require the longest residence times in the interval. The operations of solid feeding (i) and discharging (ii) to the reactor may be continuous or in step-wise mode when handling batches of Ca-containing solids, as long as the residence time of the solids in the reactor is provided (iii).

[0015] Other adiabatic moving bed reactors to carry out other gas-solid reactions, in particular lime shaft kilns for limestone calcination as they use similar materials, give important guidelines on preferred embodiments of this invention. The estimation of axial temperature and gas concentration profiles of a countercurrent moving bed reactor can be carried out with reactor-design equations, once the effective kinetics of carbonation are experimentally determined for a given local concentration of CO.sub.2, particle size, open porosity and specific surface area of the Ca-containing solids. It can be shown that the countercurrent gas-solid arrangement and the exothermic carbonation of the solids tends to generate a high temperature reaction zone, reaching a maximum T.sub.max that is located towards the axial central region of the reactor. For a vertical reactor, solids fed at the top of the reactor, move downwards by gravity and heat up in contact with the hot gases evolved in the carbonation reaction zone. Solids are discharged at the bottom of the reactor after being cooled down due to the contact with the gases coming up towards the reaction zone. Preheating and cooling of gas and solid reactants is known to be effective in lime kilns, therefore a preferred embodiment of the method uses Ca-containing solids having an effective particle diameter or thickness between 10 to 100 mm and their residence time in the reactor is between 1-20 hours. These ranges of particle diameters or thickness and residence times will be shown to be most adequate to achieve at least 80% of CO.sub.2 capture efficiency on gases containing volume fractions of CO.sub.2 higher than 0.02.

[0016] When applying the method at close to atmospheric pressure, it is important for maximizing

the CO_2 capture efficiencies that the operating conditions of the method are such as to avoid the maximum temperature in the central carbonation region to exceed $T_{max}>700°$ C., because the CO_2 partial pressure of CO_2 at such temperature is 0.03 atm (and increases rapidly with temperature, with 0.08 atm at 750° C.). It is also important that the conditions are such as to avoid $T_{max}<600°$ C., because at lower temperatures the utilization of the sorbent (defined in the state of the art as X_{max} or maximum CO_2 conversion of the Ca material at the end of the kinetically fast carbonation period) is lower than 0.5. The value of T_{max} depends among other factors on the inlet temperature of the flue gas entering the carbonator and the CO_2 content. In the case of CaO, the high enthalpy of carbonation demands that the volume fraction of CO_2 does not exceed 0.1. Such volume fraction limit is 0.125 for $Ca(OH)_2$ because of its lower carbonation enthalpy. In contrast, for volume fractions of CO_2 below 0.02 it would be necessary to feed the gases at increasingly high temperatures approaching the target T_{max} being close to the 650° C., usually considered optimum carbonation temperature in the state of the art.

[0017] The solutions of the mass and energy balances in the countercurrent carbonator reactor that will be provided below indicate that when the Ca-solid is CaO, the optimum objective of 600° C. $<T_{max}<700°$ C. is achieved when the gas is a flue gas with CO_2 volume fraction between 0.02 and 0.1, and the inlet temperature of the gas follows a proportionality rule given by a value of 560° C.$\pm$40° C. when the volume fraction is 0.02 and a value of ambient temperature $\pm$10° C. when the volume fraction is 0.1.

[0018] When the solids are $Ca(OH)_2$, the optimum objective of 600° C.$<T_{max}<700°$ C. is achieved when the gas is a flue gas with CO_2 volume fraction between 0.04 and 0.12, and the inlet temperature follows a proportionality rule given by a value of 550° C.$\pm$30° C. when the CO_2 volume fraction is 0.04, and a value of ambient temperature$\pm$10° C. when the volume fraction is 0.12. When the solids are a mixture of CaO and $Ca(OH)_2$, the optimum objective of 600° C.$<T_{max}<700°$ C. is achieved when the inlet gas temperature and CO_2 concentration follow the proportionality rules of the previous two sentences in proportion to the molar fractions of CaO and $Ca(OH)_2$.

[0019] The solution of mass and heat balances in the countercurrent moving bed carbonator also indicate that when treating gases volume fraction of CO_2 lower than 0.125, as indicated in the previous paragraphs, the difference between the gas temperature at the exit of the reactor and T_{max} becomes smaller. Therefore, a preferred embodiment of this method, when the incoming gas requires a heat input to put it at the correct inlet temperature to be able to make T_{max} between 600-700° C., is further characterized in that the gas discharged from the reactor enters a heat exchanger to supply heat to the gas fed to the reactor.

[0020] When the solids are CaO, moving in countercurrent mode respect to a gas with CO_2 volume fraction between 0.1 and 0.25 the method is further characterized by the spraying of water at the high temperature region located in the central part of the reactor, to limit the maximum carbonation temperatures, T_{max}, to between 600-700° C., preferably around 650° C. Note that this action of spraying water is needed even if the temperature of the gas entering the carbonator is at ambient temperature.

[0021] In another preferred embodiment with the same objective (i.e. cooling the central carbonation region in the reactor) the gas is a flue gas with CO_2 volume fraction between 0.1 and 0.25, the method is further characterized by the mixing of the flue gas with ambient air to bring the resulting gas mixture to the conditions described above for CO_2 volume fraction lower than 0.1.

[0022] Similarly as above, the methods of cooling by spraying water and/or by diluting the inlet gas with air are applied when the solids are $Ca(OH)_2$ or mixture of CaO and $Ca(OH)_2$, depending on the cooling requirements as illustrated in the examples and detailed description below.

[0023] To facilitate rapid scale up, methods described in the previous paragraphs use as much as possible mechanical similarities with current lime kilns. Therefore, all methods described so far using countercurrent carbonator reactors are further characterized by an inlet gas velocity at the gas entrance of the reactor between 0.5-1 m/s measured at normal conditions. This choice supports the assumptions of effective heat transfer between the gases and the solids moving in countercurrent mode that allows for the high energy efficiencies during the CO_2 capture by carbonation from solids at close to ambient temperature, and having to produce carbonated solids also at a temperature close to the ambient.

[0024] As noted above, the equilibrium of CO_2 on CaO does not allow for high CO_2 capture efficiencies when the concentration of CO_2 in the gas is low (i.e. below the threshold marked in previous paragraphs at a CO_2 volume fraction of 0.02). Therefore, operation of the method targeting maximum temperatures in the carbonation zone, T_{max}, below 100° C. are preferred for gases with volume fraction of CO_2 lower than 0.02, where it is known in the state of the art that $Ca(OH)_2$ can achieve high carbonation conversion under the right reaction conditions and gas-solid contact times. In these conditions, $Ca(OH)_2$ is also the preferred material and operating conditions must be such as to have in the central carbonation region of the reactor a high relative humidity in the gas while avoiding the formation of liquid water that could flood the $Ca(OH)_2$ pore network, drastically slowing down the carbonation rates and making the method impractical. After investigating materials and reaction conditions as described below, a preferred embodiment of the method is when the gas is air at ambient temperature, where the solids are $Ca(OH)_2$, preferably with a surface area higher than 30 m^2/g, the gas is a flue gas with volume fraction between 0.005 and 0.04 and temperature between ambient temperature and 70° C. further characterized by water spraying at the gas inlet and in the central part of the reactor carbonation zone to maintain maximum temperatures below 70° C. and relative humidity between 80-100%.

[0025] In a similarly preferred embodiment, the gas is humidified air at ambient temperature, with CO_2 content between 400-500 ppmv, or vitiated air or flue gases at close to ambient temperature with a CO_2 content between 500 to 5000 ppmv and relative humidity between 80-100%, entering the reactor at 5-10 m/s, and the solids are $Ca(OH)_2$ preferably with a surface area higher than 30 m^2/g, contained in the form of honeycombs, extruded bricks, plates or bags with a geometry to allow an effective depth of the carbonated layer of 1-10 mm. The emphasis on high velocities and solid forms offering low pressure drop is necessary to accommodate the vast flows of air required to capture meaningful flow rates of CO_2 for climate change mitigation purposes. The use of known porous solids in the method of this invention, in a form that cannot entrain into the gas, facilitates CO_2 capture devices from ambient air with a lower footprint (i.e., lower cross-sections). Indeed, a preferred embodiment that will make the method more economical and energy efficient is when the porous Ca-containing solids are fed to the moving bed carbonator reactor device in an extruded or molded form so that the $CaCO_3$ containing solid product is a cured product that can enter the market of prefabricated construction materials. This is because the cost and energy dedicated for extruding and shaping the Ca-containing solids would no longer be allocated to the method to capture CO_2, as they would be recovered from the sales of the product and the substitution of existing market products with intense energy consumption and higher carbon footprint.

[0026] Optionally, the method further comprises a step of estimation of a residence time required to achieve the target carbonation conversion of the Ca-containing solids.

[0027] When the range of CO_2 concentrations in the inlet gas is between 500 ppmv (air) to 25% v, and the temperature between of CO_2 between 20-650° C. $T_{g,in}$ and, the step of estimation of a residence time required to achieve the target carbonation conversion of the Ca-containing solids comprises the following steps: [0028] a step of estimation, from the carbon mass balance, of the flow of solids to capture the targeted flow of CO_2 from the inlet gas; [0029] a

step of calculation of a first energy balance to estimate the outlet temperature $T_{g,out}$ of the gas depleted in CO_2 generated in the reactor leaving the reactor as sensitive heat in the gas depleted in CO_2 assuming that the carbonated solids leave the reactor at the same temperature as the gas at the inlet gas enters the reactor; [0030] a step of calculation of a second energy balance to estimate a maximum temperature T_{max}, attainable in a carbonation zone located in a central part of the reactor, considering the outlet temperature $T_{g,out}$ of the gas depleted in CO_2 of the step of calculation of the first energy balance, and assuming that the solids leave the reactor at the inlet temperature of the gas, i.e.: $T_{s,out}=T_{g,in}$. [0031] a step of estimating a required length of the carbonation zone with a kinetic model for such temperature for the chosen properties of the Ca-containing solid acting as CO_2 sorbent.

[0032] The method of this invention requires of particular carbonator reactors. In a preferred embodiment, such device to carry out the methods described above dealing with CO_2 volume fractions higher than 0.02 are characterized by a supply line of Ca-containing solids containing CaO or $Ca(OH)_2$ of mixture thereof, a discharge line of $CaCO_3$ containing solids, a supply line of gas containing CO_2 connected to the discharge line of $CaCO_3$-containing solids and a discharge line of gas depleted in CO_2 that is connected to the supply line of Ca-containing solids to the reactor. The Ca-containing solids move downwards by gravity in a moving bed of solids that is kept under adiabatic conditions by a refractory wall covered by a wall. There are means to control the charge and discharge rate of solids, such as solid valves, to set a residence time of the solids at between 1-20 hours.

[0033] In another preferred embodiment, the device to carry out the methods described above dealing with CO_2 volume fractions lower than 0.02 are characterized by a supply line of $Ca(OH)_2$, a discharge line of $CaCO_3$ containing solids, a supply line of air or vitiated air connected to the discharge line of $CaCO_3$-containing solids and a discharge line of air depleted in CO_2 that is connected to the supply line of Ca-containing solids to the reactor. Ca-containing solids move from one end to the other of the device, or the device wall has means to move respect to the solids. The rate of charge and discharge of solids in and out the reactor allows the control of the residence time of the solids at between 20-200 hours. The need to accommodate large flow rates of air to capture meaningful quantities of CO_2 from the atmosphere, demands for preferred embodiments where this device has a cross-section between 0.1 to 0.2 times the flow rate in Nm^3/s, and the bed porosity is between 0.6-0.8, so as to minimize pressure drop while maintaining sufficient inventory of solids in the reactor to sustain residence times between 20-200 hours.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

[0034] A set of drawings is attached wherein, with illustrative and non-limiting character, the following has been represented:

[0035] FIG. **1**A: general scheme of the method of this invention comprising a moving bed reactor of Ca-containing solids (white circles) containing CaO or $Ca(OH)_2$ that moves downwards while contacting with a gas moving upwards. The exothermic carbonation of the solids generates a central carbonation reaction region, where both gas with CO_2 and the Ca-containing solids arrive preheated in gas-solid heat exchange zones by the carbonated solids and the gas depleted in CO_2, respectively. FIG. **1**B: Qualitative plot of axial temperature profiles in the adiabatic moving bed reactor of FIG. **1**A.

[0036] FIG. **2**A. Model simulation results of the axial concentration profiles of CO_2 in the gas phase (solid lines) and carbonate molar fraction (dotted lines) in a countercurrent (11.3 m long) carbonator reactor. FIG. **2**B. Model simulation results of the axial concentration profiles of

CO.sub.2 in the gas phase (solid lines) and carbonate molar fraction (dotted lines) in a cocurrent (25 m long) carbonator reactor.

[0037] FIG. **3**. Plots of carbonate conversion vs time in Ca-containing solids of Ca(OH).sub.2 and CaO and effective particles diameters (d.sub.p) of 2 and 10 cm using the shrinking core model with control of CO.sub.2 gas diffusion through the open porosity of the external carbonated layer of the Ca-containing solids.

[0038] FIG. **4**. Experimental plots of molar conversion to CaCO.sub.3 during carbonation of CaO (after one calcination from limestone) at different temperatures (from Y. Criado et al. 2018).

[0039] FIG. **5**. Solutions of the heat balance to achieve a maximum temperature, T.sub.max=650° C., in the autothermal carbonation region of the reactor in a countercurrent reactor, as a function of initial CO.sub.2 volume fraction and inlet gas temperature.

[0040] FIG. **6**. Method using the heat content in the product gas depleted in CO.sub.2 to preheat the inlet gas.

[0041] FIG. **7**. Method using spraying water to cool the carbonation zone.

[0042] FIG. **8**. Method using air to reduce the CO.sub.2 content in the inlet gas and reduce the maximum temperature of the autothermal carbonation zone.

[0043] FIG. **9**. Representation of the extruded Ca-containing solids of Ca(OH).sub.2 used in Example 2.

[0044] FIG. **10**. Experimental carbonation conversion vs time of CaO in dry air (0% relative humidity, RH) and in 95% RH at 65° C. 20 mg of sample in a thermogravimetric analyzer.

[0045] FIG. **11**. Experimental carbonation conversion vs time of Ca(OH).sub.2 in dry air (0% RH) and other RH values at 65° C. and 5% v of CO2. 11-12 mg of sample in a thermogravimetric analyzer.

[0046] FIG. **12**. Experimental carbonation conversion vs time of Ca(OH).sub.2 at different temperatures. Bed of commercial high surface Ca(OH).sub.2 in the form of a dry mortar pellet of 1.5 cm diameter and height embedded in a crucible with only the top surface exposed to the gas. 12% v CO.sub.2 saturated in water vapour (100% RH).

[0047] FIG. **13**. Experimental and predicted values of the depth of the carbonated layer in a Ca-containing solids of Ca(OH).sub.2 when exposed to ambient air (450-550 ppmv) at 40-60% RH and temperature between 18 and 22° C.

[0048] FIG. **14**. Experimental crushing strength measured at different molar conversion to CaCO.sub.3 of dry Ca(OH).sub.2 cylindrical porous pellets of 5.5 mm diameter and height, carbonated when exposed to ambient air (450-550 ppmv) at 100% RH and temperature between 18 and 22° C.

[0049] FIG. **15**. Method of this invention to capture CO.sub.2 from humid air.

PREFERRED EMBODIMENTS OF THE INVENTION

[0050] The main characteristics of the method disclosed in this invention are conceptually represented in FIG. **1**A. The objective of the method is to capture the CO.sub.2 that is diluted in gas. Ca-containing solids (**5**) containing active CaO and/or Ca(OH).sub.2 (**1**) are known to be able to carbonate at optimum temperatures between 600-700° C. in contact with the CO.sub.2 to form CaCO.sub.3, reaching maximum calcium molar conversions between 0.5 to 0.7 when the specific surface area of the solids is higher than 10 m.sup.2/g, so as to allow sufficient build-up of a thin carbonate layer in the interior of the Ca-containing solids. On the other hand, porous Ca(OH).sub.2 is also know to carbonate up to calcium molar conversions exceeding 0.9, even in ambient air, in particular when relative humidity is higher than 80%. Taking into account these optimum carbonation conditions, different preferred embodiments of this method are defined, depending on the CO.sub.2 concentration and temperature of the gas to be treated, so that optimum conditions are reached in the carbonator reactor used for efficient CO.sub.2 capture by carbonation.

[0051] Preferred embodiments of the method apply to the capture of CO.sub.2 from a flue gas, or other industrial gas with CO.sub.2 concentrations between 2-25% v, targeting a carbonation

temperature between 600°−700° C. in the central region of the carbonator. For applications where the flue gas is emitted at less than 200° C. from an industrial source, and the Ca-containing solids are being transported at ambient temperature to the capture site, a first challenge is to reach said targeted carbonation temperature in the carbonation zone. It will be shown below that countercurrent gas-solid contact mode of the method of this invention allow the definition of certain operating windows that can reach said optimum carbonation temperatures using only the heat released during carbonation. This is therefore highly energy efficient, as no other external sources of energy are needed to preheat incoming reactant streams, and leads to highly compact reactor designs resembling high energy efficient lime kilns, that have similar gas-solid heat exchange or preheating zones (**10**, **30**), a first preheating zone (**10**) and a second preheating zone (**30**). In this context, the countercurrent gas flow arrangement in the carbonator reactor (**100**) is an essential feature of the method disclosed in this invention, because it can be demonstrated that an autothermally generated carbonation zone (**20**) at high temperature can reach said optimum temperatures for the effective capture of the CO_2 by the carbonation of the Ca-containing solids located in such zone. This is because a preheating zone (**10**) at the top of the reactor (**100**) is formed, where the solids (**1**) coming in at ambient temperature are heated by the gas depleted in CO_2 (**4**) flowing upwards from the carbonation zone (**20**) at high temperature of the reactor (**100**). Similarly, the reactor (**100**) comprising an inlet gas (**3**) wherein the gas is preheated in a region (**30**) by contacting with the high-temperature solids leaving the carbonation zone (**20**) at high temperature, preferably a central region, of the reactor (**100**) and, as a result, the solids abandoning the reactor (**100**) are cooled down, as needed in applications where the carbonated solids (**2**) are disposed or transported to a centralized regeneration plant to obtain pure CO_2 from decomposition of $CaCO_3$. FIG. **1**B includes a qualitative description of the axial temperature profiles in the reactor (**100**) used in the method of this invention, for a case where the heat carrying capacity of the gas (expressed as the product of mass flow rate of gas and heat capacity $(mCp)_g$) is larger than the heat carrying capacity of the solids (expressed as $(mCp)_s$).

[0052] To undertake a quantitative demonstration of the benefits of the method of the present invention, and to select the preferred embodiments and methods for this invention, a simplified moving bed reactor model has been solved, together with dedicated experiments and simulations to characterize the characteristic operating conditions in the method to reach optimum reaction conditions in the carbonation zone (**20**) at high temperature. The main assumptions to build quantitative estimations of reactor (**100**) performance are as follows: [0053] The reactor is adiabatic and both gas and solids move in plug flow in countercurrent mode. [0054] Heat transfer between solids and gases is of sufficient quality so that temperature difference between gas and solids is assumed to be negligible inside the reactor (**100**), with step changes in temperature between gas-solid heat exchange or preheating zones (**10**, **30**) and carbonation zone (**20**) at high temperature. [0055] The rate of carbonation reaction follows the shrinking core model, controlled by the diffusion of CO_2 through the gas phase occupying the voids in the external carbonated layers of the Ca-containing solids, with an effective diffusivity of CO_2 that is the product of the diffusion coefficient of CO_2 at the temperature of the Ca-containing solids (estimated from Perry's handbook correlations) and the porosity of the carbonated layer of the Ca-containing solids. [0056] The molar conversion of $Ca(OH)_2$ to $CaCO_3$ is assumed to be 0.6 in the external layer of carbonated Ca-containing solids, when the carbonation temperature is between 600-700° C. (i.e. consistent with maximum carbonation conversion of lime resulting from a first calcination of limestone, as reported in the state of the art of Calcium Looping CO_2 capture systems). The molar conversion is assumed to be 0.9 (see FIGS. **10-12**) when the solids are $Ca(OH)_2$ and the temperature of operation is below 100° C. and the relative humidity above 80%.

[0057] Using the previous set of assumptions, it is possible to solve the mass and energy balances in the three main zones (**10**, **20**, **30**) of the reactor (**100**) of FIG. **1**A, to identify thermodynamic

constrains (i.e., limits to the reaction by the known equilibrium equations of CO_2 on CaO leading to inefficient utilization of the sorbent by incomplete carbonation in the carbonation zone (**20**) at high temperature). Also, to target optimum operating conditions as a function of inlet gas (**3**) compositions and temperatures and Ca-solid characteristics (mainly diameter, porosity and composition of the Ca-containing solids).

[0058] When the kinetics of carbonation are known, the model allows to calculate the length of the carbonation zone (**20**) at high temperature, as the product of the superficial velocity of the moving solids and the residence time needed to achieve a targeted CO_2 solid conversion. FIG. **2**A shows an example of the reactor model capabilities to predict the axial CO_2 concentration profile in the gas and the solid conversion profile assuming the kinetic of FIG. **3**. FIG. **2**B shows similar predictions when the method uses a cocurrent gas-solid contact mode at the same assumed temperature of carbonation (650° C. in this particular example) and at the same boundary conditions. The length of the carbonation zone (**20**) at high temperature is 11.3 m long when using a countercurrent gas-solid mode and 25 m long when using a cocurrent moving bed reactor, indicating an additional advantage of the countercurrent gas-solid contact mode of the carbonator reactor used in this invention.

[0059] FIG. **3** shows an example of predictions from the shrinking core kinetic model used to solve the reactor model used for FIG. **2**A. These examples are based on a well-known control of the progress of carbonation by Fick's diffusion law in porous Ca-materials of large diameter (i.e., characteristic carbonation lengths>1 cm) at optimum temperatures of carbonation of 650° C. As shown in the example, Ca-containing solids having an effective particle diameter or thickness between 10 to 100 mm are able to reach their carbonation conversion close to their maximum (0.5-0.7 at temperatures between 600-700° C.) when in contact with a wide range of CO_2 content in the gas, as long as there is gas-solid contact time of between 1-30 hours.

[0060] FIG. **4** shows experimental results of carbonation of CaO derived from a single calcination of a typical limestone. FIG. **4** is also known in the state of the art, but it has been brought here to highlight the fact that in order to achieve a maximum utilization of the sorbent (i.e., maximum of molar conversion of Ca to $CaCO_3$) it is essential that temperatures in the carbonation zone (**20**) at high temperature are higher than 550°. On the other hand, note that the partial pressure of CO_2 is 0.03 atm at 700° C. and hence, CO_2 capture efficiencies will sharply decrease at temperatures exceeding 700° C. Therefore, the operating conditions of the method of this invention should be such as to be able to reach carbonation temperatures in the carbonation zone (**20**) at high temperature around 650° C. (±50° C.). The challenge is therefore to find conditions for the method adequate to achieve known optimum carbonation temperature of around 650° C. in the carbonation zone (**20**) at high temperature of FIG. **1**A.

[0061] Since the use of moving bed reactors for CO_2 capture by carbonation as in FIG. **1**A has not been disclosed before, we have solved this design problem for a wide range CO_2 concentrations in the inlet gas (**3**), i.e. between 500 ppmv (air) to 25% v, and temperature between 20-650° C. $T_{g,in}$, following the following procedure: [0062] Estimate from the carbon mass balance the flow of solids (**1**) to capture the targeted flow of CO_2 from the inlet gas (**3**). Preferably, this has been done considering between 80-90% capture efficiency for industrial applications and 50% for CO_2 capture from air, and considering that all the heat generated in the reactor must leave the adiabatic reactor as sensible heat in the gas depleted in CO_2 (**4**), $T_{g,out}$. [0063] Solve a first energy balance to estimate the outlet temperature of the gas depleted in CO_2 (**4**) generated in the reactor leaving the adiabatic reactor as sensible heat in the gas depleted in CO_2 (**4**). This is because in all capture applications considered in this invention the heat carrying capacity of the gases (expressed as the product of mCp in FIG. **1**B) is much larger than the heat carrying capacity of the solids. As a result, the carbonated solids (**2**) are assumed to leave the reactor at the same temperature as the gas at the inlet gas (**3**) entering the reactor (**100**). [0064] Solve a second energy balance to estimate the maximum temperature

attainable in the carbonation zone (**20**) at high temperature, T.sub.max, considering that T.sub.g.out is known from the previous calculation point, and assuming that the solids leave the reactor (**100**) at the inlet temperature of the gas T.sub.s,out=T.sub.g,in. As it is the case for other moving bed reactors undertaking exothermic reactions, the solution of such heat balance reveals that the temperature in the carbonation zone could escalate to values well above 700° C. under many conditions (i.e., inlet flows of gases with high CO.sub.2 content and temperatures) if no other restrictions are applied (such as equilibrium). [0065] Once the temperature T.sub.max in the carbonation zone (**20**) at high temperature is calculated, the required length of the carbonation zone (**20**) at high temperature can be estimated with the kinetic model for such temperature (see example in FIG. **3**), for the chosen properties of the Ca-containing solid acting as CO.sub.2 sorbent. This allows an estimation of the residence time required to achieve the target carbonation conversion of the Ca-containing solids.

[0066] With the reactor model solved as noted above, it has been possible to generate preferred operating windows (combinations of inlet temperature and CO.sub.2 composition of the inlet gas (**3**)) to target an optimum temperature in the carbonation zone of about 650° C., that should lead to optimum utilization of the sorbent (Ca-conversions to CaCO.sub.3 between 0.5-0.7). FIG. **5** summarizes the results of such analysis for a system fed with Ca-containing solids (**1**) made with CaO or with Ca(OH).sub.2 with CO.sub.2 carbonation conversions of 0.6. Each point located in the solid lines indicate an optimum combination of inlet temperature and CO.sub.2 volume fraction in the inlet gas (**3**) entering the reactor (**100**) to reach in the carbonation zone (**20**) at high temperature, the optimum temperature of 650° C. The line on the left refers to cases where CaO is the only material in the solids (**1**) and the line on the right refers to cases where Ca(OH).sub.2 is the only material in the solids (**1**). Grey bands have been added to both lines to simply cover with a ±50° C. interval the temperatures around 650° C. and just ±10° C. interval the temperature around ambient conditions. Although the relationship is not fully linear, it is clear from this analysis when the Ca-containing solids to be carbonated are made of CaO, and the targeted gas is a flue gas with CO.sub.2 volume fraction between 0.02 and 0.1, the inlet temperature of the gas should be higher when the volume fraction of the gas is low and lower when the CO.sub.2 content of the gas is high. Indeed, the results indicate a proportionality rule given by a value of 560° C.±40° C. when the volume fraction is 0.02 and a value of ambient temperature±10° C. when the volume fraction is 0.09 to 0.1. This means that the method of this invention will generate an optimum temperature in the carbonation region of between 600-700° C. by simply preheating or cooling the inlet gas to fit the rule given above and in FIG. **5**. A similar analysis yields a similar proportionality rule, when the solids (**1**) are Ca(OH).sub.2 and the inlet gas (**3**) is a flue gas with CO.sub.2 volume fraction between 0.04 and 0.125, its inlet temperature should be adjusted to follows a proportionality rule given by a value of 550° C.±30° C. when the CO.sub.2 volume fraction is 0.04 and ambient temperature±10° C. when the volume fraction is 0.125. A similar proportionality rules could be achieved when the solids are a mixture of CaO and Ca(OH).sub.2.

[0067] Since most flue gases from energy efficient industrial processes are at mild temperatures, the capture of CO.sub.2 from such gases when CO.sub.2 content is below 8-10% v will require some preheating of the inlet gas (**3**) before it enters the reactor (**100**). On the other hand, since in the same conditions the heat released in the carbonation zone (**20**) at high-temperature comes out as sensitive heat in the decarbonized gas depleted in CO.sub.2 (**4**), a preferred embodiment of the method involves the preheating of the inlet gas (**3**) with the hot gas depleted in CO.sub.2 (**4**) in a gas-gas heat exchanger (**110**) and the mixing of the heated product gas (**41**) with ambient air (**31**) to reduce the temperature of the product gas (**42**) as indicated in FIG. **6**.

[0068] FIG. **5** also indicates that for high CO.sub.2 contents in the gas (CO.sub.2 contents higher than 9% v CO.sub.2 when using CaO and 12.5% v CO.sub.2 when using Ca(OH).sub.2), some kind of cooling below ambient temperature would be needed of the gas entering the reactor (**100**), in order to compensate for the excess of energy released during carbonation in the carbonation zone

(20) and maintain optimum carbonation temperatures in said zone (20). Since cooling of the flue gas from ambient temperature would not be energy efficient and economic, a preferred method for when the inlet gas (3) has a CO_2 volume fraction between 0.1 and 0.25, is further characterized by the spraying of water (56) at the high temperature region located in the central part of the reactor (carbonation zone (20) in FIG. 1A). The Examples below will illustrate the calculation method to of the water flow required to limit the maximum carbonation temperatures to between 600-700° C., preferably around 650° C.

[0069] In another preferred embodiment shown in FIG. 8, when the gas has a CO_2 volume fraction between 0.1 and 0.25, the method further characterized by the mixing of the flue gas at the inlet gas (3) with ambient air (33) to bring the resulting gas mixture to the CO_2 concentration conditions of described above (see FIG. 5) to reach autothermal carbonation temperatures between 600-700° C. in the carbonation zone (20).

[0070] In all preferred embodiment discussed to this point the physical and thermal properties of solids, and the characteristics of the gas-solid contact mode is similar to the mild solid and gas preheating regions in lime shaft kilns. Therefore, the teachings of such kilns can be applied to choose superficial gas velocities of the gas (3, 4) in the reactor (100) that ensure a sufficient quality in the heat transfer between gas and solids necessary to develop the preheating zones (10, 30). Attending also to the typical bed porosity between 0.4 and 0.5 of the random packed solids (1) with pellets or stone sizes distribution between 2-10 cm, the method is further characterized by an inlet gas velocity at the gas entrance of the reactor between 0.5-1 m/s measured at normal conditions, so that both pressure drop and heat transfer between gas and solids remains similar as in shaft kilns.

[0071] Regarding material's characteristics, Ca-containing solids used in the reactor (100) will be lime rocks produced from the calcination of natural limestone rocks or from recycled carbonated materials, or manufactured from powdered CaO or $Ca(OH)_2$ in the form of porous pellets or extruded, brick-type or honeycombs (200) with holes or channels (201) as shown in FIG. 9, separated by a solid wall of between 20-30 mm (allowing a depth of the carbonated layer of 10-15 mm in each side of the wall) and a bed porosity (determined in this case by the fraction of free crosssection area occupied by the holes or channels (201)) of between 0.15-0.35 sufficient to moderate the pressure drop in the reactor (100) when the gas has CO_2 concentrations between 2-25% v. The possible use of pozzolanic additives for mechanical strength and other additives to enhance porosity and mechanical strength will follow the state of the art of extruding operations of solids in fine particle form.

[0072] All preferred embodiment of this invention are valid for the use in the moving reactor of Ca-containing solids containing an intermediate mixture of CaO and $Ca(OH)_2$. The purpose of such mixture of CaO and $Ca(OH)_2$ is to achieve a more adequate average enthalpy of carbonation in the reactor so as to have an additional degree of freedom to reach temperatures for carbonation in the autothermal carbonation zone, and adapt it to the gas treated in the reactor. Such average enthalpy of carbonation will indeed range between −69 to −178 KJ/mol Ca depending on the $Ca(OH)_2$ solid molar ratio varying between 1 and 0.

[0073] When the gas contains a small concentration of CO_2 (e.g., less than 2% v), the method of this invention requires inlet gas temperatures that are high and very close to optimum carbonation temperature range of 600° C.-700° C. (see FIG. 5). However, CO_2 capture efficiencies will be low under such conditions because, even if the gas depleted in CO_2 (4) abandoning the reactor (100) has a concentration of CO_2 at equilibrium with CaO, such concentration will be close to the inlet concentration (note that the equilibrium concentration of CO_2 on CaO is 0.01 at 650° C. and 0.03 atm at 700° C.). Therefore for gases with volume fraction of CO_2 lower than 0.02, the method of this invention will preferably target carbonation temperatures in carbonation zone (20) below 100° C., where it is known in the state of the art that $Ca(OH)_2$ can achieve high carbonation conversion under the right reaction conditions and gas-solid contact times. Preferred methods are defined below considering a slow

motion of solid in such applications, so as to allow the Ca-containing solids to reach a high carbonation degree despite the low CO_2 concentrations in the gas.

[0074] Dedicated experiments have been carried out to characterize the kinetics of carbonation of suitable porous $Ca(OH)_2$ pellets under the conditions expected when applying the method of this invention. First, some test CaO materials (see FIG. **10**) confirmed that CaO does not directly carbonate at a useful rate of reaction in contact with a dry gas with CO_2. It is however able to react when the gas contains water vapour, because then the CaO converts first to $Ca(OH)_2$ using ambient humidity (as shown in FIG. **10** at 65° C. and 95% relative humidity) and then $Ca(OH)_2$ carbonates (as shown in FIG. **11**). Furthermore, as indicated in FIG. **11**, dedicated experiments with $Ca(OH)_2$ in powdered form in a thermogravimetric analyzer (11-12 mg of sample, T=65° C., 5% v CO_2 and the rest air) revealed the importance of relative humidity (RH in the figure) to both accelerate the carbonation rate and maximize the final value of molar carbonation conversion. These screening test also confirmed the superiority regarding higher carbonation rates and higher maximum conversions of commercially available $Ca(OH)_2$ materials with surface area higher than 30 m^2/g, because the product layer of $CaCO_3$ formed on $Ca(OH)_2$ surfaces also have a detrimental effect on rate of carbonation and maximum carbonate conversion.

[0075] Despite these restrictions, when $Ca(OH)_2$ is simply mixed with water to make a mortar of $Ca(OH)_2$, the resulting $Ca(OH)_2$ porous material, after drying in air at 110° C., is able to carbonate in humid CO_2 contained air (as shown for FIG. **12**). FIG. **12** is only one illustrative example of such results, for a particular pellet of dry $Ca(OH)_2$ mortar embedded in a crucible of 1.5 cm diameter and height to expose just the top side to 12% v CO_2 and the rest air saturated in humidity and track the progress of the carbonation reaction front with time. As can be seen, the experimental curves of Ca molar conversion vs. time are almost identical for three different values of temperature (20, 55 and 80° C. in this particular experiment), as long as relative humidity is high (100% in this experiment for all cases). A shrinking core model is observed in the photograph by spraying a phenolphthalein solution (1% weight in ethanol) to dye with colour the unconverted core of $Ca(OH)_2$ while the region rich in $CaCO_3$ remains uncolored. As FIG. **13** indicates, the experimentally measured depth of the carbonated layer in these porous pellets slowly increases with time even when the pellet is carbonating under ambient air (450-500 ppmv at relative humidities between 40-60%) in reasonable agreement with Fick's diffusion law applied to the CO_2 diffusing in the pores of the external carbonated layer of the pellet (solid line in FIG. **13**, is the same kinetic model than the one used at higher temperatures in FIG. **3** but adapted to the flat geometry of the carbonation front instead of the spherical geometry of FIG. **3**). The experimental results, fitted with Fick's diffusion law applied to an shrinking core model, indicate that Ca-containing solids with a geometry such as to allow a penetration of the depth of the carbonated layer of 1-3 mm still require a residence times as high as 20-100 hours to approach 90% of their maximum conversion under the low concentration CO_2 of air. The same material exposed to flue gas atmospheres with average 5% v of CO_2 at 650° C. would allow depths of the carbonated layer to reach 10 mm in just 3 hours (see Example 2), consistent with what has been discussed around FIG. **3** for spherical particles. This means that $Ca(OH)_2$ in extruded form can also be used as Ca-containing solids in CO_2 capture from flue gases (see Example 2) with characteristic thicknesses between 1-10 mm depending on flue gas concentrations, to achieve carbonation conversions exceeding 0.9 depending on solid residence time, using reactor design methods as described above for spherical shape forms. The use of extruded forms may be justified in applications where there is market for the carbonated extruded forms (i.e. bricks for construction composed of $CaCO_3$, when the initial $Ca(OH)_2$ has been fully carbonated). The use of extruded forms also allows a substantial reduction of the reactor volume by allowing the packing of Ca-containing solids with lower bed porosities while maintaining the same gas pressure drop. This could be important in applications of the reactor of this invention in CO_2 capture process in

ships for freight transport (see Example 2).

[0076] As FIG. **14** indicates, the mechanical properties (in terms of crushing strength measured in cylindrical pellets of 5.5 mm height and diameter carbonated in humid air) of dry $Ca(OH)_2$ porous materials prepared by mixing $Ca(OH)_2$ with water to make a mortar are enhanced, making them suitable for construction applications. This is qualitatively similar to what happens with other mortar materials containing free lime or free $Ca(OH)_2$, where the Ca molar conversion to $CaCO_3$ increases with time (known in the state of the art for cementitious materials as CO_2 curing). Indeed, the use of porous of $Ca(OH)_2$ in different shapes and forms is part of the state of the art and the method of this invention uses such availability of $Ca(OH)_2$ materials to optimize the CO_2 capture efficiency when applying the method to gases with low concentrations of CO_2 (below 2% v) and at temperatures below 100° C., as long as the porous $Ca(OH)_2$ solids has a geometry of the solid such as to expose the external surface of the material to the gas and allow an effective minimum depth of the carbonated layer of 1-3 mm to be developed. For example, flat sheets of material exposed in both sides to the gas, or standard extruded bricks with holes or channels separated by a solid wall of between 2-6 mm (allowing a depth of the carbonated layer of 1-3 mm in each side of the wall) would fulfill such requirement. Therefore, in another preferred embodiment of the method of this invention, the solids entering the reactor (**1**) are porous $Ca(OH)_2$ pellets, preferably with a surface area higher than 30 m^2/g, the gas is a flue gas (**3**) with volume fraction between 0.005 and 0.04 and temperatures between ambient temperature and 70° C. further characterized by water spraying at the entrance of the gas and in the central part of the reactor carbonation region to maintain maximum temperatures below 70° C. and relative humidity between 80-100%.

[0077] In another preferred embodiment, the gas is air-humidified at ambient temperature, with CO_2 content between 400-500 ppmv, or vitiated air or flue gases at close to ambient temperature with a CO_2 content between 500 to 5000 ppmv and relative humidity between 80-100%, entering the reactor at 5-10 m/s, the solids being contained in the form of extruded honeycombs or bricks, plates or bags with an effective minimum depth of the carbonated layer of 1-3 mm.

[0078] The preferred intervals adopted in the previous paragraph come from the need to use high superficial gas velocities when targeting relevant capture flows of CO_2 for climate change mitigation purposes (i.e. requiring vast flows of air of at least 50000 Nm^3/s to capture CO_2 at a rate of 1 Mt CO_2/y). Since the molar flow of CO_2 is low when feeding to the reactor a given flow of gas (**3**) with a low concentration of CO_2, the molar flow of $Ca(OH)_2$ (**1**) to be carbonated is proportionally small and the residence time of such $Ca(OH)_2$ in the carbonation zone (**20**) can increases inversely proportional to such small solid flow, to reach values as high as 100 hours when targeting depth of the carbonated layer of 1-3 mm (see FIG. **13**). The need to moderate the pressure drop in the carbonator reactor (**100**) requires a sufficient bed porosity (0.6-0.8) and geometry (honeycombs, sheets, plates etc.) of the porous $Ca(OH)_2$. A horizontal configuration of the reactor (**100**) may be more convenient to accommodate the long reactors (see EXAMPLE 4), required for air capture, as shown in FIG. **15**.

[0079] Examples of design provided below are non-restrictive, as they are used to illustrate some particular choices of design and application of some preferred embodiments of the invention under the assumptions stated above.

EXAMPLES

Example 1. Reference Case Using CaO Ca-Containing Solids

[0080] This is an example where Ca-containing solids (**1**) of CaO are fed to the carbonator reactor (**100**) to capture a target of 50 tCO_2 per day from a typical combustion flue gas at the inlet gas (**3**) with 8.5% v fraction of CO_2 and at 157° C. Such CO_2 capture rate represents 85% of the CO_2 entering the reactor. It also fixes the flow rate of gas at 4.08 Nm^3/s at standard normal conditions (0° C., 1 atm) and the average CO_2 volume fraction between inlet and

outlet at 0.060, as obtained from the axial concentration profiles of CO_2 in the gas phase solved with the countercurrent reactor model combined as shown in FIG. **2**A, using the shrinking core model as in FIG. **3**. The porous CaO stones or pellets are assumed to have a diameter of 0.04 m and open porosity of 0.6 (which is achievable from by calcination of existing limestones or pelletized limestones with a porosity of 0.12 in the carbonate). When fully carbonated, they are assumed to reach a maximum calcium molar conversion of 0.60. This is also the carbonate content in the external carbonated shell of the lime stones or pellets as soon as they start carbonating. A mass balance on carbon fixes the flow rate of solids (**1**) at 106 t CaO/day. In these conditions, the solution of the heat balance in the CaO first preheating zone (**10**) yields a temperature for the gases at the exit of the reactor of $T_{g,out}=528°$ C. The previous inlet conditions have been chosen as to translate in the generation of an autothermal high-temperature carbonation zone (**20**) in the central part of the reactor (**100**) with a maximum temperature, T_{max}, identical to 650° C. considered in the state of the art as optimum for carbonation. Conveniently, this temperature is lower than the equilibrium temperature for $CaCO_3$ decomposition at the point with the lowest CO_2 partial pressure in the reactor (i.e., at the exit) when capturing 85% of the CO_2 (which means in this case a CO_2 concentration at the exit of 0.014 being the equilibrium at T_{Max} of 0.01). However, higher capture efficiencies are to be expected, as certain carbonation could occur in the first preheating zone (**10**) as the equilibrium at $T_{g,out}$ is of only 0.0004 atm. [0081] By fixing the gas velocity at 1 m/s at normal gas inlet conditions, the cross-section of the reactor results in 4.08 m^2. The length of carbonation zone provides a final design of the reactor and allows the estimation of the pressure drop. To determine the length of the carbonation reaction zone, it is necessary to establish the time required to reach 90% of carbonation conversion in the CaO, as adopted in the reference design at the average CO_2 concentration found by the solids in their movement countercurrent respect to the gas. To construct the conversion vs time curve of FIG. **3**, the diffusivity of CO_2 in air is calculated at 650° C. (yielding $1.13 \cdot 10^{-4}$ m^2/s) and the porosity of the carbonated layer forming in the exterior of the Ca-containing solids is calculated to be 0.28 from the initial assumed porosity (0.6) and the molar densities of $CaCO_3$ and CaO. In these conditions, the shrinking core model for spheres predicts 8.31 hours to reach 90% of the maximum carbonate conversion in the Ca-containing solids (i.e., an average molar conversion of 0.60 in the Ca-containing solids). Therefore, to ensure such residence time of the Ca-containing solids in the carbonation zone (**20**) of the reactor it is necessary that the volume of the carbonation zone (**20**) at high temperature is 45.9 m^3, considering a bed porosity of 0.4, or 11.3 m of reactor reaction zone height. The Ergun's equation predicts a pressure drop of just 0.20 atm in such region, at the gas velocity of 3.4 m/s at the inlet temperature conditions of the carbonation reaction region.

[0082] Note that the previous example is non-restrictive and the skilled in the art will know how to adapt it to many other applications. There is a large margin to adapt the design of the reactor to the specific characteristic of the Ca-containing solids. For examples: Ca-containing solids with an effective diffusion coefficient of CO_2 in the Ca-containing solids that is ¼ than the assumed gas diffusion coefficient of CO_2 in air, will have to have ½ of the diameter of the Ca-containing solids assumed above to maintain identical conversion vs time curve in the shrinking core model. An interest outcome from this design exercise, is that there is a practical limit for the initial porosity of the CaO Ca-containing solids, and high porosity materials are favoured as long as they maintain suitable reactivity and crushing strength to be handled in moving beds. For example, for a maximum calcium molar conversion of 0.60 when carbonating active CaO from a single calcination cycle, a porosity CaO of 0.46 would require two orders of magnitude longer residence time (and hence reactor volume) to achieve the same objectives of capture than those described in the example. Reducing the activity of the material (i.e., to lead to maximum carbonation conversions below 0.5) would solve the pore plugging limit, but would translate into a less effective use (conversion) of the solids to carbonate, which is not optimum if the method is applied

to capture CO.sub.2 from disperse industries requiring transport of the sorbent. Low maximum conversion of the Ca-containing solids (as it happens with highly cycled particles in standard Calcium Looping systems) could only be a practical solution for CO.sub.2 capture when the source of CO.sub.2 (the emitter of the gas at the inlet gas (**3**)) is near to the calciner plant required to produce pure CO.sub.2 and CaO from the carbonated material.

[0083] Another interest outcome from this example is that there is a CO.sub.2 concentration limit for the gas entering the reactor: higher concentrations of CO.sub.2 will lead to higher adiabatic maximum temperatures calculated in the auto-thermally generated carbonation zone (**20**) at high temperature. For this example, it can be seen such adiabatic temperature is calculated to be 722° C. in this example when the CO.sub.2 content at the inlet gas (**3**) is 9.5% v. According to the equilibrium of CO.sub.2 on CaO, the concentration of CO.sub.2 in the gas phase would not go below 4.7% v at such temperature in such region, thereby reducing the capture efficiency and/or the effectiveness of the reactor as a reactor, as increasing volumes of reactor at such equilibrium temperature would become inactive for CO.sub.2 capture. In the case of treating gases with CO.sub.2 volume fractions higher than 9% v using the referred solids and conditions, the methods of cooling by spraying water (FIG. **7**) or by diluting the inlet gas with air should be applied (FIG. **8**). In this example, to cool the carbonation zone to 650° C. when the CO.sub.2 content at the inlet gas (**3**) is 9.5% v, a 0.05 kg/s of liquid water (**56**) at ambient temperature is required to be sprayed in the carbonation zone (**20**) at high temperature, or 0.45 Nm.sup.3/s of air (**33**) to be diluted into the inlet gas to reduce the CO.sub.2 fraction to 8.5% v. Similar proportionality rules for higher CO.sub.2 contents in the inlet gas (**3**) could be achieved.

Example 2. Reference Case Using Ca(OH).SUB.2 .Ca-Containing Solids

[0084] This example has been chosen to illustrate a similar design exercise as in Example 1, when the Ca-containing solids is porous Ca(OH).sub.2 in the form of extruded, brick-type, honeycombs with holes or channels (as in FIG. **9**), being all the rest parameters as in Example 1. The lower enthalpy of carbonation of Ca(OH).sub.2 would translate into a maximum temperature in the carbonation zone (**20**) of only T.sub.Max=432° C. Since this is not optimum for maximum conversion of the solids, it is preferred in this example to feed the flue gases in the inlet gas (**3**) at higher temperatures. Therefore, heat from the gas depleted in CO.sub.2 (**4**) exiting the reactor (**100**) is supplied to the incoming flue gas at the inlet gas (**3**) in a gas-gas heat exchanger (**110**) as shown in FIG. **6**. For an average molar conversion of 0.60 in the Ca-containing solids and a temperature in the carbonation zone of T.sub.max=650° C., the flue gas (**32**) has to be pre-heated up to 373° C. before entering the reactor (**100**) yielding a temperature for the gases at the exit of the reactor of T.sub.g.out=401° C. This is sufficiently high to ensure a sufficient ΔT in the gas-gas heat exchanger (**110**). Conveniently, the incoming flue gas temperature is higher than the equilibrium temperature for Ca(OH).sub.2 decomposition in the flue gas atmosphere (assumed to have 10% v of water vapor), which is 412° C. according to Barin's equation, avoiding the possible re-hydration of the un-carbonated solids coming from the carbonation zone (**20**) at 650° C. (above the Ca(OH).sub.2 decomposition temperature in water vapor of 519° C.).

[0085] When Ca-containing solids of pure Ca(OH).sub.2 are used, the open porosity of the carbonated layer forming in the exterior of the Ca-containing solids is calculated to be 0.57 from the initial assumed porosity (0.6) and the molar densities of CaCO.sub.3 and Ca(OH).sub.2. This superior carbonated layer porosity for Ca(OH).sub.2 solids compared to CaO of Example 1 enables for lower residence times or the possibility of more compact bed arrangements, as the solids are extruded, brick-type, honeycombs with depths of the carbonated layer 0.01-0.015 m and reasonable residence times, which is a clear advantage in the use of Ca(OH).sub.2 solids instead of CaO. Said compact arrangements of extruded solids will be particularly beneficial when the carbonator is operated in a location where minimum reactor volumes will be preferable, such in a ship used for freight transport. The shrinking core model for flat surfaces predicts that 2.9 hours are needed for a maximum calcium molar conversion of 0.60 and a 0.01 m depth of carbonated layer (i.e. 0.02 m of

wall thickness). Therefore, to ensure such residence time (or average residence time in a semi-continuous feeding of batches of extruded $Ca(OH)_2$ solids) of the Ca-containing solids in the carbonation zone (**20**), a volume of the carbonation zone of 25.6 m^3, or 6.3 m of reactor height, are required for a bed porosity of 0.25 (i.e. square voids of 0.02 m, as in FIG. **9**) with a pressure drop of just 0.01 atm for such region calculated by considering the square geometry of the gas channels (**201**) and typical friction factors.

Example 3. Particular Case for Gas Polishing Applications Using $Ca(OH)_2$.Ca-Containing Solids

[0086] The method of this invention, in particular when using the ability of porous $Ca(OH)_2$ to extensively carbonate at temperatures below 100° C., allows for deep decarbonisation of gases that have a low content of CO_2. This can be valuable for many applications, in particular as a "gas polishing" option to remove CO_2 downstream of other capture systems, where approaching very high capture efficiencies ("zero emissions") is not economically viable. The very low specific cost of the sorbent material used in the method of this invention, and the mild temperatures reached in the carbonation zone when the CO_2 inlet concentration is low, allow for very large inventory of solids in the reactor. For example, for a flue gas inlet concentration of 1% vol of CO_2 at 50° C. (i.e. 6.93 Nm^3/s of flue gas target a capture of 10 tCO_2/day) and a 98.5% relative humidity (i.e. 12% vol H_2O), porous pellets of $Ca(OH)_2$ of 2.5 cm of diameter and porosity of 0.6 are used. Smaller diameter pellets than in Example 1 are convenient in this example to enhance carbonation rates at the lower CO_2 concentrations. The pellets are assumed to have a maximum calcium molar conversion of 0.81 at relative humidities (above 80% according to FIGS. **11** and **12**).

[0087] As in the previous Examples, the CO_2 capture efficiency is of 85%, meaning in this case a CO_2 concentration at the exit of just 0.15% v CO_2. From the heat balances, $T_{gas,out}$ and T_{max} of 69° C. and 71° C. are calculated, respectively. Despite the low CO_2 inlet concentration, this temperature increment would reduce the relative humidity to below 44% at the exit, thus minimizing the carbonation conversion. Therefore, to maintain maximum temperatures below 55° C. and relative humidity above 80%, liquid water is sprayed at different locations inside the reactor. To maintain relative humidity between of 80 and 97%, sprays of 0.015 kg/s at carbonation zone dimensionless heights of 0.43, 0.69, 0.86 and 0.97 are required considering the solids conversion profile in FIG. **2**A. This results in a moderate increment in T_{max} to 55° C., and $T_{gas,out}$=54° C., ensuring that relative humidity can be controlled above 80% while avoiding the condensation of liquid water that would otherwise flood the $Ca(OH)_2$ pores and drastically reduce carbonation rates. According to the shrinking core model used to describe the carbonation kinetics of these porous solids, about 17.5 hours are needed to reach a conversion of 90% in these Ca-containing solids. Such long residence time can be achieved in a reactor with a cross-section of 4.7 m^2 operated with a gas velocity of 1.5 m/s at normal conditions and 1.80 m/s at T_{max} in the carbonation zone (**20**). The length of such carbonation zone (**20**) will be 6.11 m (for a bed porosity of 0.4) and the pressure drop about 0.14 atm (i.e., similar as in Example 2).

Example 4. Particular Case for CO_2.Capture from Air Using $Ca(OH)_2$.Ca-Containing Solids

[0088] The method of this invention allows for CO_2 capture from air or from vitiated air coming out from buildings or other sources. As in Example 3, the mild temperatures reached in the carbonation zone when the CO_2 inlet concentration is extremely low, allow for very large inventory of solids in the reactor. For example, for atmospheric air with a CO_2 concentration of 500 ppmv at 20° C. (i.e. 64.6 Nm^3/s of flue gas when we target a capture of 1000 tCO_2/year) that has been saturated to a 99% relative humidity (i.e. 2.1% vol H_2O), Ca-containing solids of $Ca(OH)_2$ arranged in the form of extruded, brick-type, honeycombs with 6 mm of thickness (i.e., 3 mm of depth of the carbonated layer) with a solids porosity of 0.6 and a

bed porosity of 0.7 (i.e., square voids of 30 mm length) to moderate the pressure drop accounting for the larger flow of atmospheric air to be treated when compared to higher CO_2 contents as in Example 2. Ca-containing solids are assumed to have maximum calcium molar conversion of 0.90 at relative humidities (above 80% according to FIGS. **11** and **12**).

[0089] A modest CO_2 capture efficiency of 50% is assumed considering the extremely low CO_2 exit concentration. From the heat balances, $T_{gas,out}$ and T_{max} of just 21° C. are calculated respectively ensuring relative humidity above 90% when the CO_2 containing air is saturated in humidity before entering the carbonation reaction zone as shown in FIG. **15**. According to the shrinking core model for flat plates, about 103 hours are needed to reach a complete conversion of these Ca-containing solids. Such long residence time can be achieved in a reactor with a cross-section of 6.5 m^2 operated with a gas velocity of 10 m/s at normal conditions. The length of such carbonation zone (**20**) will be 12.7 m and the pressure drop just about 0.024 atm.

[0090] Note that there is a large margin to adapt the design of the reactor to the specific characteristic of the ppmv CO_2 in the air. For example, vitiated air containing 2000 ppmv CO_2 will simply require ¼ the cross-section area and ¼ the residence time in the reactor when all the rest parameters are maintained.

Claims

1. A method for capturing the CO_2 from a gas entering a thermally insulated packed bed reactor of calcined Ca-containing solids, composed of CaO, $Ca(OH)_2$ or mixtures thereof capable to react to form $CaCO_3$ and obtain a gas depleted in CO_2 at a reactor gas exit; wherein the Ca-containing solids are arranged in the form of porous Ca-containing solids, such as lime rocks, extruded bricks or plates made with mortars, or in powder form inside porous bags; said Ca-containing solids having internal porosities connected to the exterior surface of the solids ranging between 0.45-0.7 and internal surface areas higher than 10 m^2/g, the method comprising the following steps: i. feeding the Ca-containing solids at ambient temperature to the reactor gas exit at a molar rate of 1-2 times the molar rate of CO_2 contained in the gas, ii. discharging the $CaCO_3$-containing solids from a gas inlet of the reactor, such that a countercurrent movement of the gas respect to the solids is generated; and iii. providing a residence time of the solids in the reactor between 1-200 hours.

2. The method according to claim 1 wherein the Ca-containing solids are CaO, the gas is a flue gas with CO_2 volume fraction between 0.02 and 0.1, and an inlet temperature of the gas follows a proportionality rule given by a value of 560° C.±40° C. when the CO_2 volume fraction is 0.02, and a value of ambient temperature±10° C. when the CO_2 volume fraction is 0.1.

3. The method according to claim 1, wherein the solids are $Ca(OH)_2$ and the gas is a flue gas with CO_2 volume fraction between 0.04 and 0.12, and an inlet temperature follows a proportionality rule given by a value of 550° C.±30° C. when the CO_2 volume fraction is 0.04, and ambient temperature±10° C. when the CO_2 volume fraction is 0.12.

4. The method according to claim 1 wherein the solids (**1**) are a mixture of CaO and $Ca(OH)_2$, the gas is a flue gas with CO_2 volume fraction between 0.02 and 0.1, and an inlet gas temperature and CO_2 concentration follows a proportionality rule given by a value of 560° C. ±40° C. when the CO_2 volume fraction is 0.02, and a value of ambient temperature±10° C. when the CO_2 volume fraction is 0.1, for CaO, and the gas is a flue gas with CO_2 volume fraction between 0.04 and 0.12 and the inlet gas temperature and CO_2 concentration follows a proportionality rule given by a value of 550° C.±30° C. when the CO_2 volume fraction is 0.04, and a value of ambient temperature±10° C. when the CO_2 volume fraction is 0.12, for $Ca(OH)_2$.

5. The method according to claim 2 further comprising a heat exchanging step wherein the gas

discharged from the reactor enters a heat exchanger to supply heat to the gas fed to the reactor.

6. The method according to claim 1, wherein the gas has a CO_2 volume fraction between 0.1 and 0.25, and the method further comprises a step of spraying water at a carbonation zone located in a central part of the reactor.

7. The method according to claim 1, wherein the gas has a CO_2 volume fraction between 0.1 and 0.25, and the method further comprises a step of mixing the flue gas with ambient air.

8. The method according to claim 1 wherein an inlet gas velocity at the gas inlet of the reactor is between 0.5-1 m/s measured at normal conditions.

9. The method according to claim 1 further comprising a step of estimation of a residence time required to achieve the target carbonation conversion of the Ca-containing solids.

10. The method according to claim 9, wherein the range of CO_2 concentrations in the inlet gas is CO_2 volume fraction between 0.02 and 0.25, and the temperature between of CO_2 between 20-650° C. $T_{g,in}$ and wherein the step of estimation of a residence time required to achieve the target carbonation conversion of the Ca-containing solids comprises the following steps: a step of estimation, from the carbon mass balance, of the flow of solids to capture the targeted flow of CO_2 from the inlet gas; a step of calculation of a first energy balance to estimate the outlet temperature $T_{g,out}$ of the gas depleted in CO_2 generated in the reactor leaving the reactor as sensitive heat in the gas depleted in CO_2 assuming that the carbonated solids leave the reactor at the same temperature as the gas at the inlet gas enters the reactor; a step of calculation of a second energy balance to estimate a maximum temperature T_{max}, attainable in a carbonation zone located in a central part of the reactor, considering the outlet temperature $T_{g,out}$ of the gas depleted in CO_2 of the step of calculation of the first energy balance, and assuming that the solids leave the reactor at the inlet temperature of the gas, i.e.: $T_{s,out}=T_{g,in}$. a step of estimating a required length of the carbonation zone with a kinetic model for such temperature for the chosen properties of the Ca-containing solid acting as CO_2 sorbent.

11. The method according to claim 1, wherein the Ca-containing solids have an effective particle diameter or thickness between 10 and 100 mm.

12. The method according to claim 1, wherein the Ca-containing solids are $Ca(OH)_2$ extruded forms with characteristic thickness between 1 and 10 mm.

13. The method according to claim 3 further comprising a heat exchanging step wherein the gas discharged from the reactor enters a heat exchanger to supply heat to the gas fed to the reactor.

14. The method according to claim 4 further comprising a heat exchanging step wherein the gas discharged from the reactor enters a heat exchanger to supply heat to the gas fed to the reactor.