



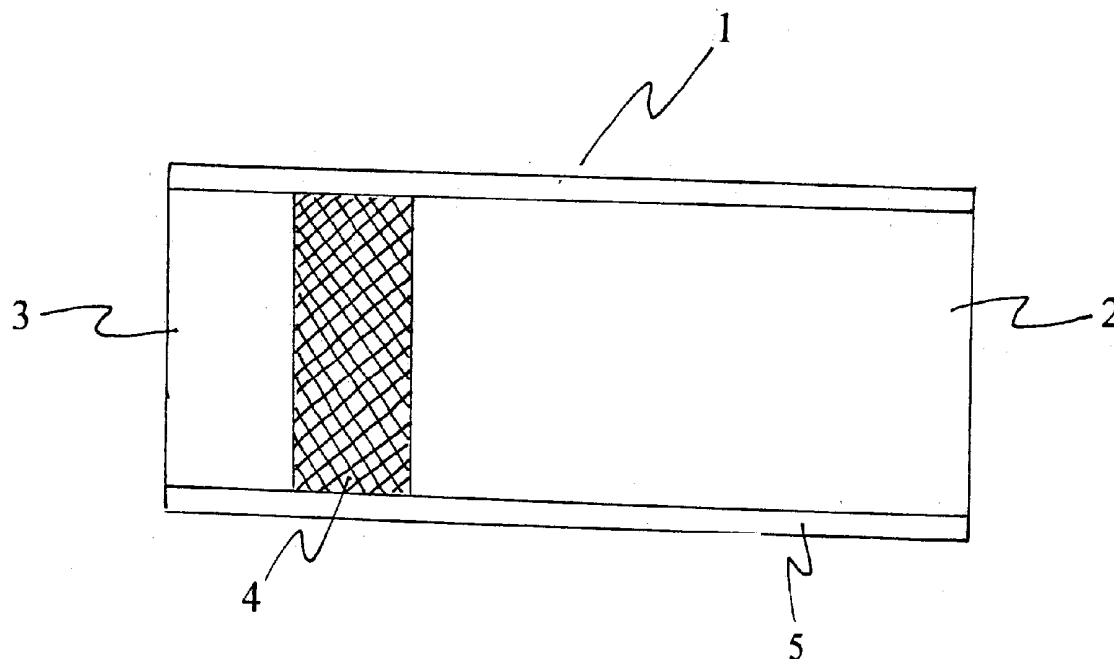
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(19) **United States**(12) **Patent Application Publication** (10) **Pub. No.: US 2004/0144251 A1**
Mitsuda (43) **Pub. Date: Jul. 29, 2004**(54) **DEVICE FOR ABSORBING CARBON DIOXIDE, AND A METHOD FOR ABSORBING CARBON DIOXIDE****Publication Classification**(51) **Int. Cl.⁷** **B01D 53/02**(52) **U.S. Cl.** **95/139; 96/108**(75) **Inventor: Hisateru Mitsuda, Kyoto (JP)**

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WESTERMAN, HATTORI, DANIELS & ADRIAN, LLP**1250 CONNECTICUT AVENUE, NW****SUITE 700****WASHINGTON, DC 20036 (US)**(73) **Assignee: INTERNATIONAL ENVIRONMENTAL CONSERVATIVE ASSOCIATION, INC., Los Angeles, CA**(21) **Appl. No.: 10/352,856**(22) **Filed: Jan. 29, 2003**(57) **ABSTRACT**

The present invention relates to a device for absorbing carbon dioxide, which is equipped along an automobile exhaust pipe and a factory chimney. The present invention also relates to a method for absorbing carbon dioxide. According to the present invention, there is provided a device for absorbing carbon dioxide, comprising a housing 4 of a material having air permeability; a cement composition for absorbing carbon dioxide, enclosed inside the housing 4; and a pipe 5 across the housing, the pipe having an inlet 2 and an outlet 3. According to the present invention, when a gas is introduced from the inlet 2, carbon dioxide in the gas is absorbed by the carbon dioxide absorbing materials such as a cement composition enclosed in the housing 4. The gas is discharged from the outlet 3.



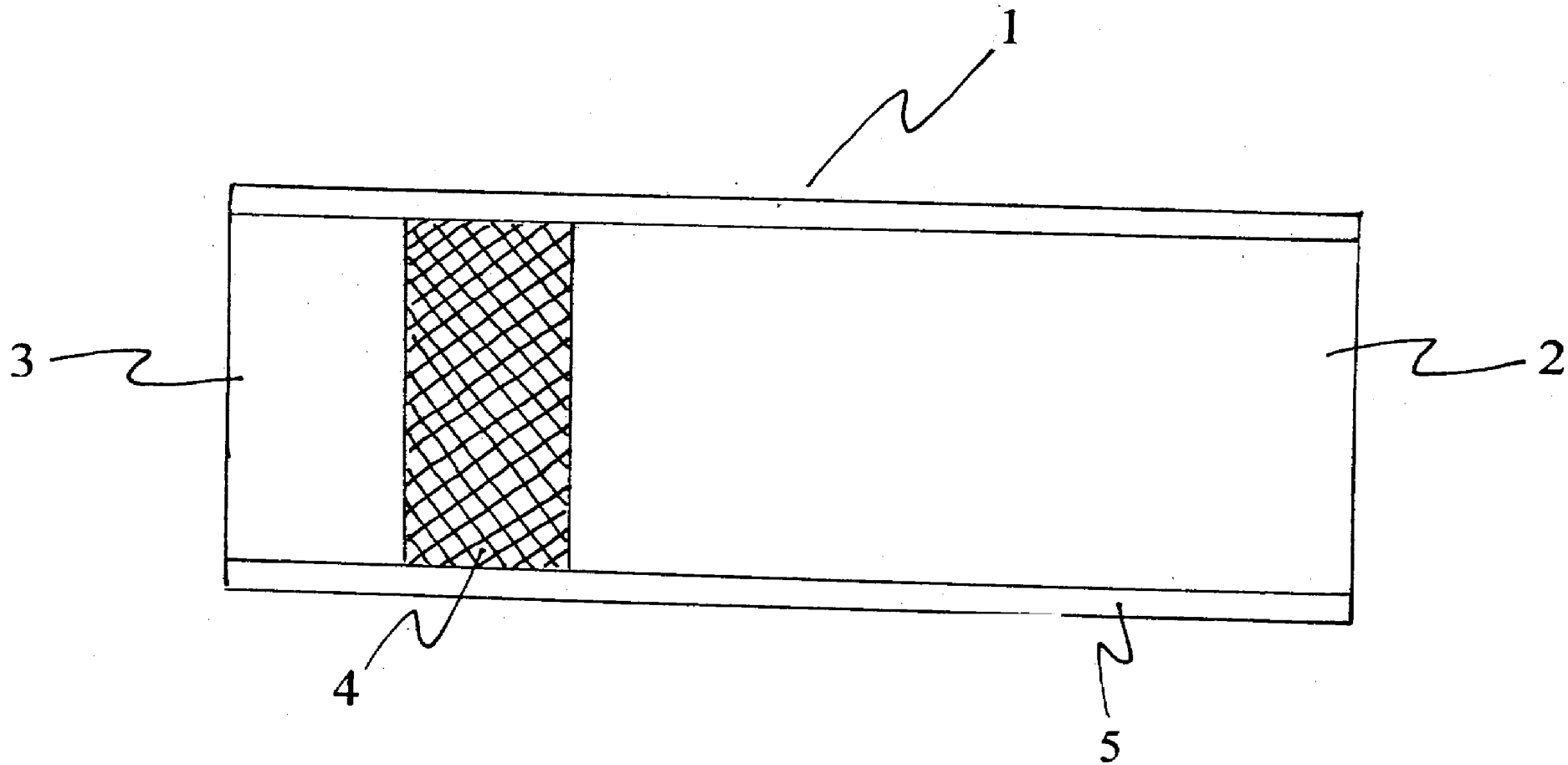


Fig. 1

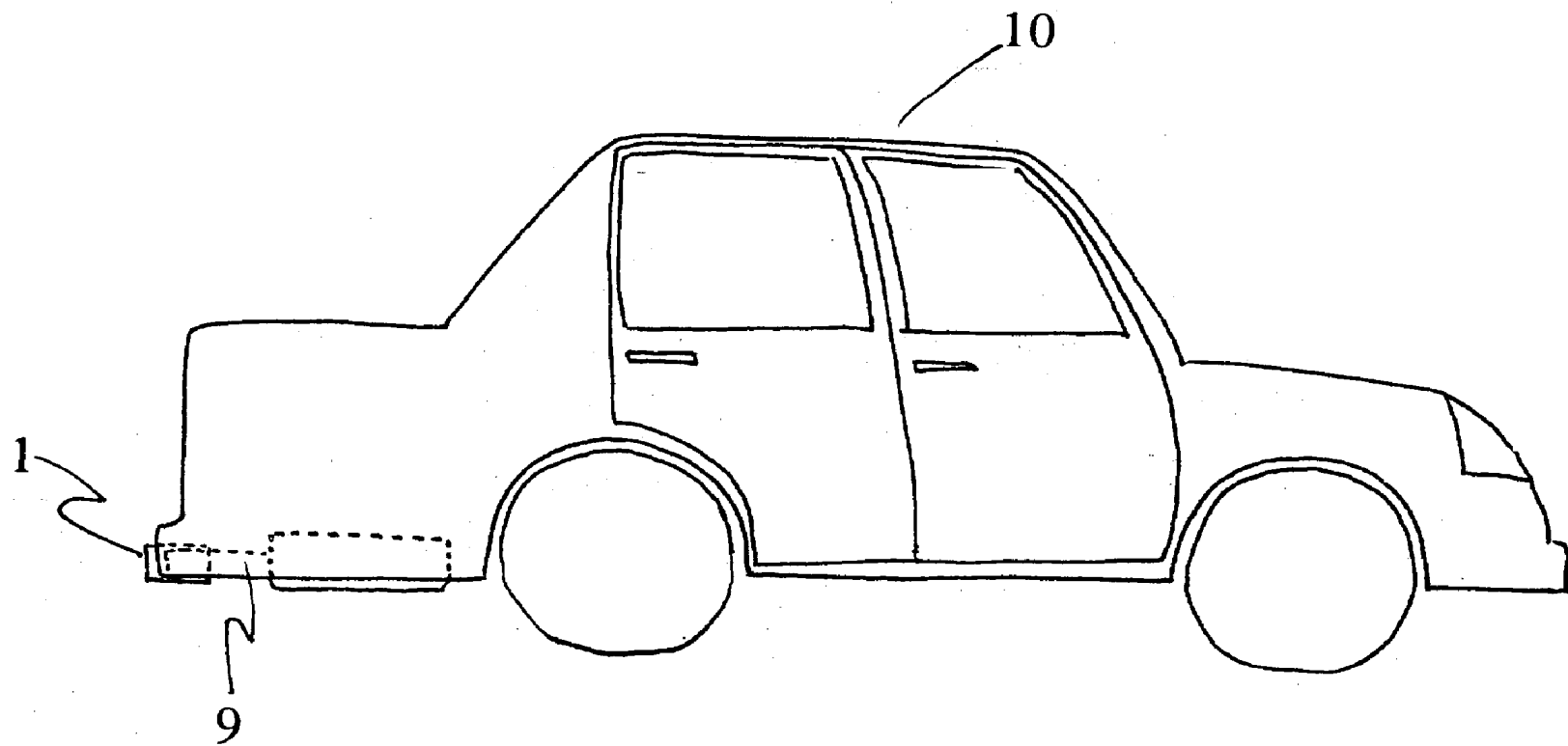


Fig. 2

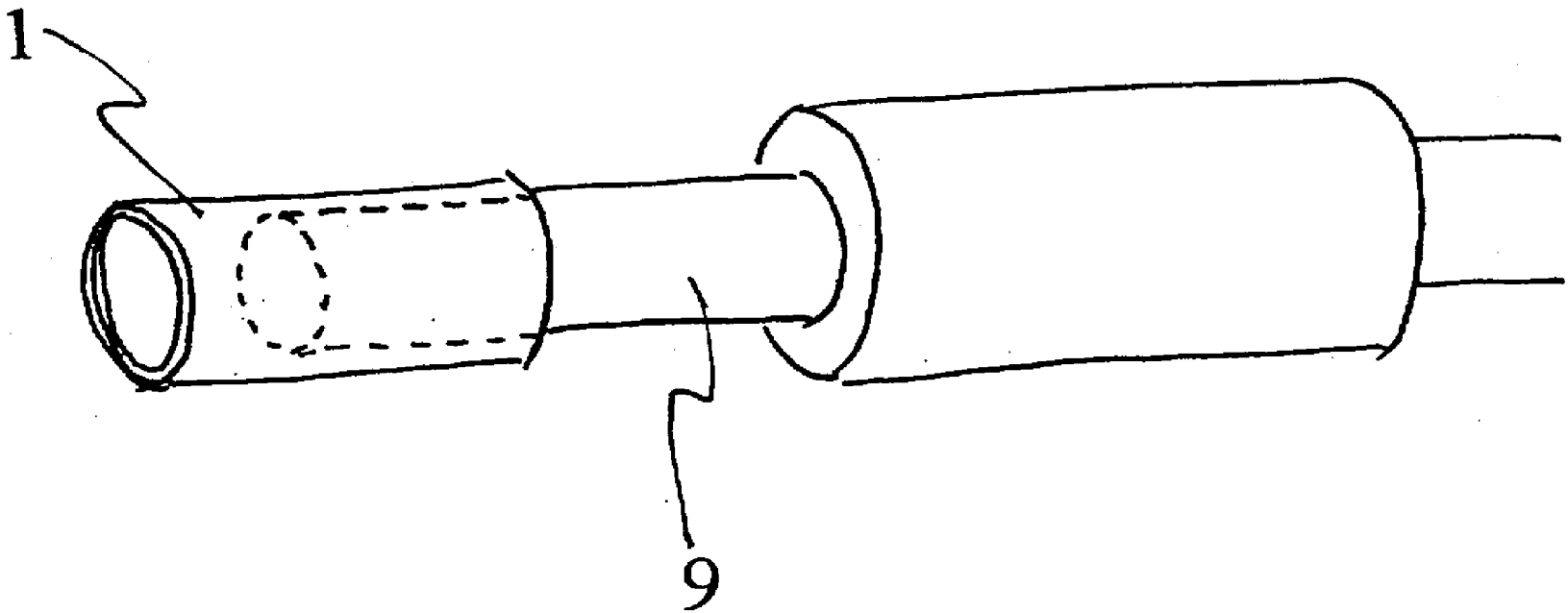


Fig. 3

DEVICE FOR ABSORBING CARBON DIOXIDE, AND A METHOD FOR ABSORBING CARBON DIOXIDE

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a device for absorbing carbon dioxide, which may be equipped on an automobile exhaust pipe or a factory chimney. The present invention also relates to a method for absorbing carbon dioxide.

RELATED ART

[0002] The stemming of the warming of the Earth is one of the most difficult objectives to be solved. The average temperature of the Earth has been recently rising gradually. If it continues, the icebergs in the south and north poles will be melted, significantly raising the sea level, resulting in the submerging of many islands and properties. In addition, the concomitant breakdown of the Earth's ecology would affect the creatures including human beings. The cause of the warming of the Earth is said to be the recent increase of the amount of carbon dioxide discharged.

[0003] The objectives of the present invention are to absorb carbon dioxide and to reduce its amount discharged, resulting in contributing to stem the warming of the Earth.

SUMMARY OF THE INVENTION

[0004] The inventor of the present invention has researched to solve the objective to stem the warming of the Earth, and then, found a carbon dioxide absorbing material such as a cement composition. According to the present invention, there is provided a device for absorbing carbon dioxide, comprising a housing of a air permeable material; and a carbon dioxide absorbing material enclosed inside the housing. According to the present invention, when a gas is passed through the housing, carbon dioxide in the gas is absorbed. The housing may be placed inside a pipe having an inlet and an outlet.

[0005] In addition, there is provided a method for absorbing carbon dioxide. The method comprises the steps of the follows: providing a housing of a air permeable material; enclosing a carbon dioxide absorbing material inside the housing; and passing a gas through the housing to absorb carbon dioxide in the gas.

BRIEF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 shows a cross sectional view of the device to absorb carbon dioxide according to the present invention.

[0007] FIG. 2 shows a view where the device of the invention is equipped at the end of an exhaust pipe of an automobile.

[0008] FIG. 3 shows a magnified view of the present invention equipped at the end of an exhaust pipe of an automobile.

DETAILED DESCRIPTION OF THE INVENTION

[0009] FIG. 1 shows a device 1 to absorb carbon dioxide according to the present invention. As shown in FIG. 1, the device 1 for absorbing carbon dioxide has a housing 4 of an

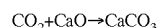
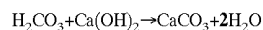
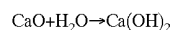
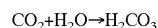
air permeable material. The housing 4, as shown FIG. 1, is a net. Alternatively, the housing may be made of, for example, a woven or non-woven sheet or paper having air permeability. Inside the housing 4, a carbon dioxide absorbing material, such as a cement composition, is enclosed. The housing 4 is placed inside a pipe 5. The pipe 5 has an inlet 2 and an outlet 3. The device, as shown in FIG. 1, is equipped along an exhaust pipe 9 of an automobile 10, as shown in FIGS. 2 and 3. Alternatively, the device may be equipped along a chimney and so on. The device is intended to absorb carbon dioxide. When an exhaust gas from the automobile 10 or chimney is introduced from the inlet 2 of the pipe 5, carbon dioxide in the exhaust gas is absorbed by the carbon dioxide absorbing material enclosed inside the housing 4. After such treatment, the exhaust gas is discharged from the outlet 3. According to the present invention, the exhaust gas efficiently contact with the carbon dioxide absorbing material. The pipe has several hooks inside the surface, to engage it with the housing 4.

[0010] In addition, on the outlet 3 of the pipe 5, a filter may be provided to trap the powder of the cement composition leaked from the housing 4.

[0011] Next, a carbon dioxide absorbing material according to the present invention is explained in detail. As the carbon dioxide absorbing material, a cement composition is preferable to use. According to the present invention, the cement composition may be selected from the group consisting of aluminous cement, magnesia cement, silica cement, Portland cement, blast furnace cement, fly ash cement, slag cement, sulfate resisting cement, high early strength cement, ultra high early strength cement, moderate heat of hardening cement, white cement, expansive cement, and the mixture thereof. Especially, it is preferable to use a Portland cement.

[0012] According to the present invention, the carbon dioxide absorbing material may include CaO in addition to SiO₂, Al₂O₃, Fe₂O₃, MgO, Na₂O, SO₃ and so on, which is not limited.

[0013] According to the present invention, the carbon dioxide absorbing material may include CaO, which is considered to mainly play a role to absorb carbon dioxide. The mechanism for the cement composition to absorb carbon dioxide is not scientifically clarified. The inventor considers that one of the dominant mechanisms is as follows. However, it should be noted that the presumed mechanism is not limited to the present invention, even if it will be tuned out to be wrong.



[0014] In the mechanism, water (H₂O) is necessary for CaO to absorb carbon dioxide. However, too much water will adversely affect the efficiency of the absorption of carbon dioxide, since water solidifies the cement composition. Therefore, the content of water in the carbon dioxide absorbing material, or cement composition, is controlled as little as possible. Generally, it is unnecessary to add water into the cement composition since the exhaust gas from automobiles or factories already include water to the extent to promote the reactions shown in the above formula.

[0015] The carbon dioxide absorbing material may include CaO. The content of CaO in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of CaO is 40 to 80% by weight, and especially 55 to 70% by weight, and more especially 60 to 67% by weight.

[0016] According to the present invention, the carbon dioxide absorbing material may include SiO₂. The content of SiO₂ in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of SiO₂ is 5 to 50% by weight, and especially 13 to 30% by weight, and more especially 17 to 25% by weight.

[0017] According to the present invention, the carbon dioxide absorbing material may include Al₂O₃. The content of Al₂O₃ in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of Al₂O₃ is 1 to 20% by weight, and especially 2 to 10% by weight, and more especially 3 to 8% by weight.

[0018] According to the present invention, the carbon dioxide absorbing material may include Fe₂O₃. The content of Fe₂O₃ in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of Fe₂O₃ is 0.1 to 15% by weight, and especially 0.3 to 10% by weight, and more especially 0.5 to 6% by weight.

[0019] According to the present invention, the carbon dioxide absorbing material may include MgO. The content of MgO in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of MgO is 0.001 to 10% by weight, and especially 0.01 to 7% by weight, and more especially 0.1 to 5.5% by weight.

[0020] According to the present invention, the carbon dioxide absorbing material may include Na₂O and/or K₂O. The content of Na₂O and/or K₂O in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of Na₂O and/or K₂O is 0.01 to 5% by weight, and especially 0.05 to 3% by weight, and more especially 0.5 to 1.3% by weight.

[0021] According to the present invention, the carbon dioxide absorbing material may include SO₃. The content of SO₃ in the carbon dioxide absorbing material is not limited in the present invention, but it is preferable that the content of SO₃ is 0.01 to 7% by weight, and especially 0.1 to 5% by weight, and more especially 1 to 3% by weight.

[0022] In the case of using a cement composition as the carbon dioxide absorbing material, the cement composition is preferably in a form of powder. The cement composition used in the present invention preferably has an averaged particle size between 0.1 and 100 μ m. According to the present invention, the housing is preferably made of net having air permeability. The net has a mesh size smaller than the average of the particle size of the cement composition. Instead, the housing may be made of alternative material discussed before. In order to trap the cement composition leaked from the net, the device of the present invention further comprises a filter provided on the outlet. According to the present invention, the housing enclosing the carbon dioxide absorbing material, and especially cement composition, preferably has a thickness of 1 to 100 mm. The device of the present invention is preferably equipped along the exhaust pipe of an automobile or along a chimney, so as to absorb carbon dioxide.

[0023] Next, examples are shown, which are contemplated by the inventors as best modes, but the present invention is not limited thereto. Those skilled in the art may modify the example within the scope of the invention defined by the claims.

EXAMPLE 1

[0024] As the carbon dioxide absorbing material, following cement composition was provided.

[0025] CaO in an amount of 60 to 67% by weight,

[0026] SiO₂ in an amount of 17 to 25% by weight,

[0027] Al₂O₃ in an amount of 3 to 8% by weight,

[0028] Fe₂O₃ in an amount of 0.5 to 6% by weight,

[0029] MgO in an amount of 0.1 to 5.5% by weight,

[0030] Na₂O and/or K₂O in an amount of 0.5 to 1.3% by weight, and

[0031] SO₃ in an amount of 1 to 3% by weight.

[0032] The cement composition was in the form of powder. The cement composition was enclosed in a net having a mesh smaller than the average particle size of the cement composition.

[0033] The net including the cement composition was placed inside a bottle having an atmosphere including carbon dioxide in a high concentration. After 1 hour, the carbon dioxide concentration was decreased by 72%, approximately.

EXAMPLE 2

[0034] The net including the ceramic composition prepared in Example 1 was placed inside a pipe to form a device to absorb carbon dioxide according to the present invention. Then, the device was equipped at the end of an exhaust pipe of an automobile.

[0035] The amount of the discharge of carbon dioxide was measured. The result proved that the device of the present invention could absorb carbon dioxide and significantly decrease the concentration of carbon dioxide in the discharged exhaust gas.

EXAMPLE 3

[0036] The net including the ceramic composition produced in Example 1 was placed inside a pipe to form a device to absorb carbon dioxide according to the present invention. Then, the device was equipped at the end of chimney of a chemical factory.

[0037] The amount of the discharge of carbon dioxide was measured. The result proved that the device of the present invention could absorb carbon dioxide and significantly decrease the concentration of carbon dioxide in the discharged exhaust gas.

What is claimed is:

1. A device for absorbing carbon dioxide, comprising:

a housing of an air permeable material; and

a carbon dioxide absorbing material enclosed inside the housing; wherein a gas is passed through the housing to absorb carbon dioxide in the gas.

2. A device for absorbing carbon dioxide according to claim 1, wherein the carbon dioxide absorbing material is a cement composition.

3. A device for absorbing carbon dioxide according to claim 1, wherein the carbon dioxide absorbing material is selected from the group consisting of aluminous cement, magnesia cement, silica cement, Portland cement, blast furnace cement, fly ash cement, slag cement, sulfate resisting cement, high early strength cement, ultra high early strength cement, moderate heat of hardening cement, white cement, expansive cement, and the mixture thereof.

4. A device for absorbing carbon dioxide according to claim 1, wherein the carbon dioxide absorbing material is a Portland cement.

5. A device for absorbing carbon dioxide according to claim 1, wherein the carbon dioxide absorbing material comprises:

CaO in an amount of 60 to 67% by weight,

SiO₂ in an amount of 17 to 25% by weight,

Al₂O₃ in an amount of 3 to 8% by weight,

Fe₂O₃ in an amount of 0.5 to 6% by weight,

MgO in an amount of 0.1 to 5.5% by weight,

Na₂O and/or K₂O in an amount of 0.5 to 1.3% by weight, and

SO₃ in an amount of 1 to 3% by weight.

6. A device for absorbing carbon dioxide according to claim 1, wherein the cement composition is in a form of powder.

7. A device for absorbing carbon dioxide according to claim 1, wherein the carbon dioxide absorbing material has an average particle size between 0.1 and 100 μ m.

8. A device for absorbing carbon dioxide according to claim 5, wherein the housing is made of a net having a mesh size smaller than the average of the particle size of the cement composition.

9. A device for absorbing carbon dioxide according to claim 1, wherein the housing enclosing the cement composition has a thickness of 1 to 100 mm.

10. A device for absorbing carbon dioxide according to claim 1, further comprising a pipe across the housing, the pipe having an inlet and an outlet, wherein when a gas is introduced from the inlet, carbon dioxide in the gas is absorbed by the carbon dioxide absorbing material, followed by that the gas is discharged from the outlet.

11. A device for absorbing carbon dioxide according to claim 10, further comprising a filter provided on the outlet for trapping the carbon dioxide absorbing material.

12. A device for absorbing carbon dioxide according to claim 1, wherein the device is equipped along the exhaust pipe of an automobile.

13. A device for absorbing carbon dioxide according to claim 1, wherein the device is equipped along a chimney.

14. A method for absorbing carbon dioxide, comprising:

providing a housing of a air permeable material;

enclosing a carbon dioxide absorbing material inside the housing; and

passing a gas through the housing to absorb carbon dioxide in the gas.

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(54) **CO₂-Sorpative Pellets and Uses Thereof**

(57) CO₂ sorptive pellets and/or granules and their use for removing CO₂ from CO₂-containing gases and for producing hydrogen. CO₂ sorptive pellets are suitable for use in fixed bed reactors and the like due to sufficient crush strength. CO₂ sorptive granules are suitable for moving, ebullated, expanded and fluidized beds. The CO₂ sorptive pellets and/or granules comprise calcium

oxide and/or magnesium oxide and at least one binding agent such as calcium titanate, calcium aluminate, calcium zirconate, magnesium titanate, magnesium aluminate, and magnesium zirconate. A method for making the CO₂-sorptive pellets is described. The CO₂ sorptive pellets optionally comprise at Ni, Pd, Pt, and/or Rh.

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Description

BACKGROUND

[0001] Calcium oxide (lime), magnesium oxide, and mixtures of calcium and magnesium oxides (dolomite) are prime candidates for removing and recovering CO₂ from hot flue gases. They are also candidates for enhancing reforming of hydrocarbons with steam by removing and recovering CO₂ from the process gas stream. Calcium and/or magnesium oxides react with CO₂ and form carbonates. The reaction is reversible, and the carbonate can be regenerated to liberate CO₂ and again form the respective oxide.

[0002] The removal of CO₂ from hot flue gases and enhancement of hydrocarbon reforming by removing CO₂ involve cyclic operations. For example, in a first step of CO₂ removal from hot flue gases, CO₂ is sorbed by a hot bed of calcium and/or magnesium oxide, forming a carbonate. The hot bed could be a fixed bed loaded with pelleted sorbent, a fluidized bed loaded with granules, or a moving bed of pellets or granules. As used herein, a "granule" is an agglomerate of numerous particles forming a larger unit. When the bed is substantially saturated with CO₂, the spent oxide in carbonate form is regenerated in a second step by passing a purge gas such as nitrogen, air, steam or a mixture thereof through the bed, thereby desorbing or liberating CO₂.

[0003] Likewise, in a first step of a hydrogen synthesis process, largely pure hydrogen is obtained by the reaction of steam and methane (or other suitable hydrocarbon) over a hot bed of calcium and/or magnesium oxide in conjunction with a reforming catalyst. The hot bed could be a fixed bed loaded with pelleted sorbent, a fluidized bed loaded with granules, or a moving bed of pellets or granules. Calcium and/or magnesium oxide acts as a CO₂ sorbent during the reforming reaction, thereby improving the conversion of methane (or other hydrocarbon) and the production of pure hydrogen. The "spent" oxide, substantially saturated with CO₂ and in carbonate form is then regenerated by passing a gas such as nitrogen, air, steam or a mixture thereof through the bed, thereby desorbing or liberating CO₂.

[0004] Calcium and/or magnesium oxides are generally synthesized or available in powder form. Powders are generally not suitable for use in fixed bed or moving bed reactors because of an unacceptable pressure drop through the reactor. Likewise, fine powders are generally not suitable for use in a fluidized bed reactor, since larger particles are needed to promote stable fluidization at practical throughput velocities. It would therefore be desirable to convert this fine powder into granules for use in fluidized bed or moving bed reactors, or pellets or extrudates for use in a fixed or moving bed reactor. Pellets are useful to allow a reasonable pressure drop through the fixed or moving bed reactor. Pellets may also be useful for ebullated, expanded, moving or fluidized bed reactors.

[0005] Calcium and/or magnesium oxides are known to undergo a significant volumetric expansion and contraction due to cyclic sorption and desorption of carbon dioxide. Since calcium oxide and magnesium oxide are ceramics, it is difficult for them to undergo volumetric expansion and contraction without cracking and falling apart.

[0006] There are several techniques known in the literature for converting powders into pellet form. These techniques involve two distinct steps - preparing green pellets from the powder followed by consolidating the green pellets by calcinating at high temperature. The calcination step is done in a controlled manner where the temperature is increased slowly or in steps. The preparation of the green pellets, the nature of the additives and pore formers mixed with the powder may affect the pellet strength.

[0007] Likewise powder can be converted into granules by using a two step technique

- first preparing a slurry by mixing powder with a solvent such as water followed by spray drying or otherwise processing the powder to convert it into green granules. The green granules are then calcined in a controlled manner to provide the desired granules.

[0008] Because calcium and/or magnesium oxide pellets or granules undergo significant volumetric expansion and contraction during CO₂ sorption/desorption, the pellets or granules prepared by conventional techniques either fall apart within a few CO₂ sorption/desorption cycles or do not have the desired CO₂ sorption capacity. Because of the volumetric expansion and contraction, suitable calcium and/or magnesium oxide pellets or granules can't be prepared by mixing calcium oxide and/or magnesium oxide with an organic binder, converting the mixture into green pellets or granules, and calcining green pellets or granules at high temperature. These pellets or granules will swell and fell apart within a few cycles of carbon dioxide sorption and desorption.

[0009] Suitable calcium oxide and/or magnesium oxide pellets or granules can't be prepared by mixing calcium oxide and/or magnesium oxide powder with gamma or alpha alumina or zirconia powder as a binder and with or without an organic pore former, converting the mixture into green pellets or granules, and calcining green pellets or granules at high temperature. The calcium and/or magnesium present in the oxide form will react with alumina and zirconia and produce calcium and/or magnesium aluminate or zirconate. Such pellets or granules will neither have sufficient CO₂ sorption capacity nor retain their shape and size.

[0010] Since calcium and/or magnesium oxide reacts with alumina, titania or zirconia, it was thought that strong particulate material or pellets could be prepared with binders that would not react with metal oxide such as calcium and/or magnesium aluminate, calcium and/or magnesium titanate, and calcium and/or magnesium zir-

conate. Attempts have been made to prepare pellets or granules by mixing calcium oxide powder with calcium titanate or calcium aluminate powder as a binder and an organic pore former, processing the mixture into green pellets or green granules, and calcining green pellets or green granules at high temperature. However, this approach has not been successful in preparing strong and dimensionally stable CaO or MgO pellets or granules.

[0011] The use of calcium and/or magnesium oxides has thus been limited in the above mentioned applications despite their high CO₂ capacity. There are two reasons. First, pellets or granules formed heretofore do not display stable capacity for CO₂ sorption since sorption capacity decreases with only a few cycles. Second and more importantly, pellets or granules formed heretofore have not been dimensionally stable. Both pellets and granules fall apart during cyclic operation and convert into powder.

[0012] A journal article by J.C. Abanades titled "The maximum capture efficiency of CO₂ using carbonation/calcination cycle of CaO/CaCO₃" Chemical Engineering Journal, vol. 90, p. 303-306 (2002), describes modeling work that showed a significant decrease in CO₂ sorption capacity of CaO sorbent with number of sorption and desorption cycles.

[0013] Considerable progress has been made towards producing metal oxide powders with stable capacity for cyclic sorption and desorption of CO₂. Two journal articles by Li et al., describe the preparation and use of CaO-calcium aluminate granular material for cyclic sorption and desorption of CO₂. The first is "Synthesis, Experimental Studies, and Analysis of a New Calcium-Based Carbon Dioxide Absorbent," Energy and Fuels, Vol. 19, pp. 1447-1452 (2005). The second is "Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation - calcination Cycles for a New Ca-Based CO₂ Sorbent," Ind. Eng. Chem. Res., Vol. 45, pp. 1911-1917 (2006). These journal articles describe preparation of granules with CaO as a starting material. Specifically, they describe preparing granules by calcining CaO or CaCO₃ first at high temperature to produce CaO. CaO and aluminum nitrate anhydrate are then mixed with 2-propanol and distilled water. The solution is dried at 110°C and calcined at 500°C to produce a fine and porous powder containing a mixture of CaO and alumina. The powder is finally calcined in air at 900°C and ground to produce granular material of desired size. In any case the starting material for producing granules of CaO-calcium aluminate is CaO. The granules have been shown to lose CO₂ capacity with time or number of cycles. These articles therefore do not describe how to produce dimensionally stable and strong CaO-calcium aluminate pellets or granules with stable CO₂ sorption and desorption capacity.

[0014] Journal articles by Martavaltzi and Lemonidou titled "Parametric Study of the CaO-Ca₁₂Al₁₄O₃₃ Synthesis with Respect to High CO₂ Sorption Capacity and Stability on Multicycle Operation," Ind. Eng. Chem. Res.

2008, 47, 9537-9543 and "Development of new CaO based sorbent materials for CO₂ removal at high temperature," Microporous and Mesoporous Materials, Vol. 110, pp. 119-127 (2008), describe preparation and use of CaO-calcium aluminate granules for cyclic sorption and desorption of CO₂. The procedure for preparing CaO-Ca₁₂Al₁₄O₃₃ is similar to that described in the two articles by Li et al. with the exception of using calcium acetate as a precursor for CaO. Once again, the granules produced have been shown to lose CO₂ capacity with time or number of cycles. These articles therefore do not describe how to produce dimensionally stable and strong CaO-calcium aluminate pellets or granules with stable CO₂ sorption and desorption capacity.

[0015] Considerable progress has also been made to show utility of CO₂ sorbent powders for improving processes for producing hydrogen. For example, a journal article by Yi and Harrison titled "Low-Pressure Sorption-Enhanced Hydrogen Production," Ind. Eng. Chem. Res. 2005, 44, pp. 1665-1669, describes the use of a mixture of reforming catalyst and CO₂ sorbent for enhanced hydrogen production. A pre-calcined dolomite in the powder form (particle size varying from 150 to 300 microns) was used as a CO₂ sorbent. The article does not describe how to regenerate dolomite powder loaded with carbon dioxide. Furthermore, it does not describe how to produce dimensionally stable and strong CaO-calcium aluminate pellets or granules with stable CO₂ sorption and desorption capacity.

[0016] Progress has also been made in producing pellets from metal oxides. For example, a journal article by Wu, Beum, Yang and Kim titled "Properties of Ca-Based CO₂ Sorbent Using Ca(OH)₂ as Precursor" Ind. Eng. Chem. Res. 2007, 46, 7896-7899, describes the use of pellets produced by 85% CaCO₃ and 15% clay binder or 85% Ca(OH)₂ and 15% clay binder for cyclic CO₂ sorption and desorption. These pellets were shown to lose a significant CO₂ sorption capacity in just 15 cycles. No information was provided regarding dimensional stability and strength of fresh and used pellets.

[0017] U.S. Pat. Publication No. 2005/0112056, now U.S. Pat. No. 7,267,811, discloses a method for making CaO based material that is useful in adsorption-enhanced steam methane reforming process. Fine composite particles containing adsorbent phase and catalyst phase were prepared by (1) forming a precursor solution containing a liquid, precursor for an adsorbent phase and precursor for a catalyst phase, (2) atomizing the precursor solution to form precursor droplets, (3) heating the precursor droplets. The fine composite particles were then mixed with suitable support material such as alumina or titania to form pellets. A support material such as alumina or titania cannot be used to make pellets with a CaO based material because CaO will eventually react with alumina or titania and form calcium aluminate or calcium titanate. This will cause decrease in carbon dioxide capacity of CaO after only a few cycles.

[0018] A journal article by Satrio, Shanks and Whee-

lock titled "Development of a Novel Combined Catalyst and Sorbent for Hydrocarbon Reforming," Ind. Eng. Chem. Res. 2005, . 44, 3901-3911, describes the use of small spherical pellets with highly reactive lime or dolomite core enclosed within a strong and porous alumina shell impregnated with nickel catalyst for enhanced hydrogen production. The article concluded that work was continuing to improve physical strength and attrition resistance of the combined catalyst/sorbent pellets.

[0019] It has been found that conventional methods are not suitable for forming dimensionally stable pellets or granules from calcium and/or magnesium oxides. This is because calcium and/or magnesium oxides undergo a significant volumetric expansion and contraction due to the sorption and desorption of CO₂. Because of the expansion and contraction, pellets or granules, which are formed from calcium and/or magnesium oxides using conventional binders and conventional techniques such as spray drying, extrusion or pelletization of powder, fall apart within a few CO₂ sorption and desorption cycles. The use of conventional binders such as alumina, titania, and zirconia are not suitable for preparing pellets or granules from calcium or magnesium oxide as they react with them, rendering them to be ineffective in absorbing carbon dioxide. Additionally, pellets or granules prepared with conventional calcium or magnesium aluminate, titanate or zirconate binders do not have enough porosity, as they fall apart within a few carbon dioxide sorption and desorption cycles. Furthermore, the pellets or granules prepared from calcium and/or magnesium oxides using conventional binders and conventional techniques do not have sufficient crush strength to be useful in a fixed bed reactor, a fluidized bed reactor, a moving bed reactor, or an expanded bed reactor.

[0020] Industry desires pellets or granules containing calcium oxide and/or magnesium oxide which have sustained performance as well as structural and dimensional stability.

BRIEF SUMMARY

[0021] The present invention relates to aggregates (pellets and/or granules) suitable for carbon dioxide sorption, a method for making aggregates (pellets and/or granules) suitable for carbon dioxide sorption, aggregates (pellets and/or granules) made by the method, an apparatus for producing a CO₂-depleted gas from a CO₂-containing gas using the aggregates (pellets and/or granules), a process for producing a CO₂-depleted gas from a CO₂-containing gas using the aggregates (pellets and/or granules), a reactor for producing a hydrogen-containing gas using the aggregates (pellets and/or granules), and a process for producing a hydrogen-containing gas using the aggregates (pellets and/or granules).

[0022] The aggregates suitable for carbon dioxide sorption comprise: 25 to 85 mass % or 35 to 85 mass % of at least one binding agent selected from calcium titanate, calcium aluminate, calcium zirconate, magnesium

titanate, magnesium aluminate, and magnesium zirconate; and 15 to 75 mass % or 15 to 65 mass % of calcium oxide, magnesium oxide or a mixture of calcium oxide and magnesium oxide; wherein the aggregate is a pellet or a granule having a median pore diameter in a range of 500 nm (5,000 ångströms) to 5000 nm (50,000 ångströms) and a porosity in a range of 45 % to 80 % or 60 % to 75 %.

[0023] As pellets, the aggregates may have a characteristic length of 0.1 mm to 3 mm.

[0024] As granules, the aggregates may have a characteristic length of 50 microns to 3 mm, or from 75 microns to 2 mm, or from 75 microns to 1000 microns.

[0025] The aggregates may optionally comprise at least one metal selected from Ni, Pt, Rh, and Pd. The pellets or granules may comprise 0.1 to 10 mass % of at least one metal selected from Ni, Pt, Rh, and Pd.

[0026] The pellets may have a crush strength of 1 to 15 lbf/mm (4 to 67 N/mm) as determined in accordance with ASTM standard test method D 6175-03.

[0027] The pellets may have a structure wherein the crush strength of the pellet is retained within 1 to 15 lbf/mm (4 to 67 N/mm) after 50 cycles of CO₂ sorption and CO₂ desorption wherein the CO₂ sorption is by exposing the pellet to a humidified CO₂-containing gas comprising 97 to 98 vol. % CO₂ at 750°C and CO₂ desorption is by exposing the pellet to humidified air at 750°C. The humidified CO₂-containing gas may comprise 2 to 3 vol. % H₂O. The humidified air may comprise 2 to 3 vol. % H₂O.

[0028] The granules may have a structure wherein the granules retain their shape and size after 50 cycles of CO₂ sorption and CO₂ desorption wherein the CO₂ sorption is by exposing the granule to a humidified CO₂-containing gas comprising 97 to 98 vol. % CO₂ at 750°C and CO₂ desorption is by exposing the granule to humidified air at 750°C. The humidified CO₂-containing gas may comprise 2 to 3 vol. % H₂O. The humidified air may comprise 2 to 3 vol. % H₂O.

[0029] The calcium titanate may be formed by reaction of at least one calcium precursor and TiO₂ in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0030] The calcium aluminate may be formed by reaction of at least one calcium precursor and at least one of alumina, aluminum hydroxide and aluminum oxide hydroxide in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0031] The calcium zirconate may be formed by reaction of at least one calcium precursor and zirconia in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0032] The magnesium titanate may be formed by reaction of at least one magnesium precursor and TiO₂ in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0033] The magnesium aluminate may be formed by reaction of at least one magnesium precursor and at least

one of alumina, aluminum hydroxide and aluminum oxide hydroxide in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0034] The magnesium zirconate may be formed by reaction of at least one magnesium precursor and zirconia in a mixture with at least one of calcium carbonate and magnesium carbonate.

[0035] The method for making an aggregate suitable for carbon dioxide sorption comprises the steps of:

(a) preparing a mixture, the mixture comprising:

at least one of calcium carbonate and magnesium carbonate in an amount to provide the 15 to 75 mass % or 15 to 65 mass % of calcium oxide, magnesium oxide or mixture of calcium oxide and magnesium oxide in the aggregate;
at least one of a calcium precursor and a magnesium precursor in an amount to provide the 25 to 85 mass % or 35 to 85 mass % of the at least one binding agent in the aggregate;
at least one of TiO_2 , Al_2O_3 , ZrO_2 , $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$ in an amount to provide the 25 to 85 mass % or 35 to 85 mass % of the at least one binding agent in the aggregate; and
20 to 80 mass % water;

(b) forming a green aggregate from the mixture;

(c) heating the green aggregate from a first temperature to a second temperature at a first average heating rate of $0.1^\circ\text{C}/\text{minute}$ to $10^\circ\text{C}/\text{minute}$, wherein the first temperature is within a first temperature range wherein the first temperature range is between 5°C and 50°C , and

wherein the second temperature is a minimum temperature of a second temperature range, the second temperature range extending from the minimum temperature of the second temperature range to a maximum temperature of the second temperature range wherein the minimum temperature of the second temperature range is 600°C and the maximum temperature of the second temperature range is 750°C ;

(d) maintaining the green aggregate within the second temperature range for a first time period of between 15 minutes and 4 hours;

(e) heating the green aggregate from the maximum temperature of the second temperature range to a third temperature at a second average rate of $0.1^\circ\text{C}/\text{minute}$ to $10^\circ\text{C}/\text{minute}$,

wherein the third temperature is a minimum temperature of a third temperature range, the third temperature range extending from the minimum temperature of the third temperature range to a maximum temperature of the third temperature range wherein the minimum temperature of the third temperature range is 900°C and the maximum temperature of the third temperature range is 1050°C ;

(f) maintaining the green aggregate within the third temperature range for a second time period of between 15 minutes and 4 hours; and

(g) cooling the green aggregate to a fourth temperature, wherein the fourth temperature is within a fourth temperature range wherein the fourth temperature range is between 0°C and 50°C , to make the aggregate;

wherein the green aggregate is exposed to an atmosphere comprising oxygen during at least one of steps (a) through (f).

[0036] The aggregate may be a pellet and the mixture may comprise 20 to 40 mass % water.

[0037] In the method, the green aggregate may be exposed to the atmosphere comprising oxygen during all of steps (a) through (f).

[0038] The mixture may further comprise 0.1 to 10 mass % of at least one metal selected from Ni, Pt, Rh, and Pd.

[0039] The calcium precursor may be selected from CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , $\text{Ca}(\text{NO}_3)_2$ and $\text{Ca}(\text{CH}_3\text{CO}_2)_2$.

[0040] The magnesium precursor may be selected from MgO , $\text{Mg}(\text{OH})_2$, MgCO_3 , $\text{Mg}(\text{NO}_3)_2$ and $\text{Mg}(\text{CH}_3\text{CO}_2)_2$.

[0041] The apparatus for producing a CO_2 -depleted gas from a CO_2 -containing gas comprises a bed containing a plurality of the described aggregates. The bed may be a fixed bed and the aggregates may be pellets. The bed may be a fluidized bed or a moving bed and the aggregates may be granules.

[0042] The process for producing a CO_2 -depleted gas from a CO_2 -containing gas comprises:

(i) passing the CO_2 -containing gas through a bed containing a plurality of the described aggregates under conditions sufficient to sorb CO_2 and form calcium carbonate and/or magnesium carbonate with the plurality of aggregates and thereby forming the CO_2 -depleted gas;

(ii) regenerating the bed by passing a purge gas through the bed under conditions sufficient to liberate CO_2 from the plurality of aggregates and withdrawing a by-product gas comprising CO_2 from the bed; and
(iii) repeating (i) and (ii) in a cyclic manner.

[0043] The conditions sufficient to sorb CO_2 and form calcium carbonate and/or magnesium carbonate may include a temperature ranging from 600°C to 800°C , preferably 650°C to 800°C , and a pressure ranging from 1 to 100 atmospheres (1 to 100 bar).

[0044] The conditions sufficient to liberate CO_2 may include a temperature ranging 650°C to 900°C and a pressure ranging from 0.9 to 100 atmospheres (0.9 to 100 bar) or a pressure ranging from 0.9 to 2 atmospheres (0.9 to 2 bar).

[0045] The purge gas may comprise at least one of oxygen, nitrogen and/or steam. The purge gas may com-

prise at least one of nitrogen and steam and may optionally comprise oxygen. The purge gas may be air or steam.

[0046] The reactor for producing a hydrogen-containing gas comprises a bed containing CO₂-sorptive aggregates and optionally containing steam-hydrocarbon reforming catalyst in a suitable form, wherein the CO₂-sorptive aggregates are the aggregates as described herein, and wherein if the bed does not contain steam-hydrocarbon reforming catalyst then at least a plurality of the CO₂-sorptive aggregates include at least one metal selected from Ni, Pt, Rh and Pd.

[0047] The process for producing a hydrogen-containing gas comprises:

- (i) in a production step, introducing steam and a feed gas containing methane into a bed, the bed containing CO₂-sorptive aggregates and optionally containing steam-hydrocarbon reforming catalyst, wherein the CO₂-sorptive aggregates are the aggregates as described herein, and wherein if the bed does not contain steam-hydrocarbon reforming catalyst then at least a plurality of the CO₂-sorptive aggregates include at least one metal selected from Ni, Pt, Rh and Pd, reacting the methane and the steam in the presence of the at least one metal and/or the steam-hydrocarbon reforming catalyst under reaction conditions sufficient to form hydrogen, sorb CO₂ and form calcium carbonate and/or magnesium carbonate, and withdrawing a product gas comprising hydrogen from the reactor;
- (ii) in a regeneration step, regenerating the CO₂-sorptive aggregates by passing a purge gas through the bed under conditions sufficient to liberate CO₂ from the CO₂-sorptive aggregates and withdrawing a by-product gas comprising CO₂ from the bed; and
- (iii) repeating (i) and (ii) in a cyclic manner.

[0048] Optionally, the bed may additionally contain one or more metal oxides. The purpose of the metal oxides is to serve as a source of oxygen during the production step. During the production step, the metal oxide undergoes reduction to a metallic form or a metal oxide of lower valence. The metal or metal oxide of lower valence undergoes oxidation to an oxide, or an oxide of higher valence in a regeneration step.

[0049] The reaction conditions sufficient to form hydrogen, sorb CO₂ and form calcium carbonate and/or magnesium carbonate may include a temperature ranging from 350°C to 800°C or 600°C to 800°C, and a pressure ranging from 1 to 100 atmospheres (1 to 100 bar).

[0050] The conditions sufficient to liberate CO₂ may include a temperature ranging 450°C to 900°C and a pressure ranging from 0.9 to 100 atmospheres (0.9 to 100 bar) or a pressure ranging from 0.9 to 2 atmospheres (0.9 to 2 bar).

[0051] The purge gas may comprise oxygen, nitrogen, and/or steam. The purge gas may comprise at least one

of nitrogen and steam and may optionally comprise oxygen. The purge gas may be air or steam.

[0052] For the case where metal oxide is used, the purge gas may be any oxygen-containing gas, for example air, oxygen-enriched air and oxygen-depleted air. The oxygen-containing gas may further comprise nitrogen and/or steam.

[0053] The one or more metal oxides may be metallic oxides corresponding to any known non-precious metal based steam-methane reforming catalyst known in the art. The one or more metal oxides may be metallic oxides of Ni, Cu and/or Fe. The metal oxides may be unsupported or supported. The metal oxides may be supported on an inert ceramic support. The composition of the inert ceramic support may be alumina, titania, zirconia, calcium aluminate, calcium titanate, calcium zirconate or mixtures thereof.

BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

[0054]

FIG. 1 is a process flow sheet for producing a CO₂-depleted gas from a CO₂-containing gas.

FIG. 2 is a process flow sheet for the generation of hydrogen using the disclosed method, process, and reactor.

DETAILED DESCRIPTION

[0055] The articles "a" and "an" as used herein mean one or more when applied to any feature in embodiments of the present invention described in the specification and claims. The use of "a" and "an" does not limit the meaning to a single feature unless such a limit is specifically stated. The definite article "the" preceding singular or plural nouns or noun phrases denotes a particular specified feature or particular specified features and may have a singular or plural connotation depending upon the context in which it is used. The adjective "any" means one, some, or all indiscriminately of whatever quantity.

[0056] As used herein "at least a portion" means "a portion or all."

[0057] "Plurality" means two or more.

[0058] As used herein "sorption" and "sorbing" include adsorption, absorption and reversible chemical reaction.

[0059] As used herein, "calcium oxide and/or magnesium oxide" includes calcium oxide by itself, magnesium oxide by itself, and any mixture of calcium oxide and magnesium oxide.

[0060] As used herein, an "aggregate" is a clustered mass of individual particles varied in shape, and varied in size including microscopic granules. Pellets and granules are examples of aggregates.

[0061] The present invention relates to aggregates suitable for carbon dioxide sorption, a method for making

aggregates suitable for carbon dioxide sorption, aggregates made by the method, an apparatus for producing a CO₂-depleted gas from a CO₂-containing gas using the aggregates, a process for producing a CO₂-depleted gas from a CO₂-containing gas using the aggregates, a reactor for producing a hydrogen-containing gas using the aggregates, and a process for producing a hydrogen-containing gas using the aggregates.

[0062] The aggregates suitable for carbon dioxide sorption may also be referred to as CO₂-sorptive aggregates.

[0063] The aggregates suitable for carbon dioxide sorption comprise 25 to 85 mass % or 35 to 85 mass % of at least one binding agent selected from calcium titanate, calcium aluminate, calcium zirconate, magnesium titanate, magnesium aluminate, and magnesium zirconate; and 15 to 75 mass % or 15 to 65 mass % of calcium oxide, magnesium oxide or a mixture of calcium oxide and magnesium oxide; wherein the aggregate has a median pore diameter in a range of 500 nm (5,000 Å) to 5000 nm (50,000 Å) or a range of 900 nm (9,000 Å) to 4000 nm (40,000 Å) and a porosity in a range of 45 % to 80 % or 45 % to 75 %.

[0064] Median pore diameter and porosity were determined by mercury porosimetry at about 60,000 psi (about 410 MPa). Mercury porosimetry instruments and/or analysis may be provided by Micromeritics Instrument Corporation.

[0065] The lower limit for the at least one binding agent may be 25 or 30 or 35 or 40 or 45 mass %. The upper limit for the at least one binding agent may be 85 or 80 or 75 or 70 or 65 or 60 or 55 mass %. The lower limit for the calcium oxide, magnesium oxide or mixture of calcium oxide and magnesium oxide may be 15 or 20 or 25 or 30 or 35 or 40 or 45 mass %. The upper limit for the calcium oxide, magnesium oxide or mixture of calcium oxide and magnesium oxide may be 75 or 70 or 65 or 60 or 55 or 50 mass %.

[0066] The aggregate may be a pellet and the pellet may have a characteristic length of 0.1 mm to 3 mm.

[0067] A pellet is defined herein as a densely packed but porous mass formed from smaller particles. A pellet is a self-supporting body. Suitable pellets may have a characteristic length of between 0.1 mm and 3 mm. The characteristic length is defined as the volume of the pellet divided by the outside surface area of the pellet. The pellet may have any regular or irregular shape as desired. The pellet may be in the shape of a sphere, cylinder, tablet or the like.

[0068] For example, a cylinder having a radius of 0.5 mm and a length of 3 mm, has a volume of about 2.356 mm³, an outside surface area of about 11 mm², and therefore a characteristic length of about 0.214 mm. A sphere having a radius of 3 mm has a characteristic length of 1 mm.

[0069] The aggregates may be granules. The size (e.g. characteristic length) of the granules may vary from 50

microns to 3 mm, or from 75 microns to 2 mm, or from 75 micron to 1000 microns.

[0070] The aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of only one binding agent selected from calcium titanate, calcium aluminate, calcium zirconate, magnesium titanate, magnesium aluminate, and magnesium zirconate. Alternatively, the aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of more than one binding agent selected from calcium titanate, calcium aluminate, calcium zirconate, magnesium titanate, magnesium aluminate, and magnesium zirconate in combination.

[0071] As used herein, the term "calcium aluminate" means any of the various calcium aluminates, for example tricalcium aluminate (3CaO.Al₂O₃), dodecacalcium hepta-aluminate (12CaO.7Al₂O₃), monocalcium aluminate (CaO.Al₂O₃), monocalcium dialuminate (CaO.2Al₂O₃), monocalcium hexa-aluminate (CaO.6Al₂O₃), dicalcium aluminate (2CaO.Al₂O₃), pentacalcium trialuminate (5CaO.3Al₂O₃), tetracalcium trialuminate (4CaO.3Al₂O₃) and mixtures thereof. The calcium aluminate may contain a minor amount of free CaO that is not tied with alumina.

[0072] Likewise, the term "calcium titanate," "calcium zirconate," "magnesium titanate," "magnesium aluminate" and "magnesium zirconate" refers any of the various forms of the respective compounds..

[0073] The CO₂-sorptive aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of a mixture of tricalcium aluminate and dodecacalcium hepta-aluminate. The CO₂-sorptive aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of a mixture of monocalcium aluminate and dodecacalcium hepta-aluminate. The CO₂-sorptive aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of a mixture of tricalcium aluminate, monocalcium aluminate and dodecacalcium hepta-aluminate. The CO₂-sorptive aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of a mixture of monocalcium aluminate and monocalcium dialuminate. The CO₂-sorptive aggregates may comprise 25 to 85 mass % or 35 to 85 mass % of a mixture of monocalcium aluminate and monocalcium hexa-aluminate.

[0074] The aggregates may optionally comprise at least one metal selected from Ni, Pt, Rh, and Pd. The aggregates may comprise 0.1 to 10 mass % of at least one metal selected from Ni, Pt, Rh, and Pd. These metals may be added to catalyze the reforming reaction.

[0075] The aggregates may be pellets. The pellets may have any suitable crush strength. The pellets may have a crush strength of 1 to 15 lbf/mm (4 to 67 N/mm) as determined in accordance with ASTM standard test method D 6175-03.

[0076] As referred to herein, the value representing "crush strength" is determined by the American Society for Testing Materials (ASTM) Standard Test Method D 6175-03 "Standard Test Method for Radial Crush Strength of Extruded Catalyst and Catalyst Carrier Particles."

[0077] The pellets may have a structure wherein the crush strength of the pellet is retained within 1 to 15 lbf/mm (4 to 67 N/mm) after 50 cycles of CO₂ sorption and CO₂ desorption wherein the CO₂ sorption is by exposing the pellet to a humidified CO₂-containing gas comprising 97 to 98 vol. % CO₂ and 2 to 3 vol. % H₂O at 750°C and CO₂ desorption is by exposing the pellet to humidified air comprising 2 to 3 vol. % H₂O at 750°C.

[0078] The aggregates may be granules. The granules may have a structure wherein the granules retain their shape and size after 50 cycles of CO₂ sorption and CO₂ desorption wherein the CO₂ sorption is by exposing the granule to a humidified CO₂-containing gas comprising 97 to 98 vol. % CO₂ and 2 to 3 vol. % H₂O at 750°C and CO₂ desorption is by exposing the granule to humidified air comprising 2 to 3 vol. % H₂O at 750°C.

[0079] The calcium titanate may be formed by reaction of at least one calcium precursor and TiO₂ in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form calcium titanate. Reaction conditions sufficient to form calcium titanate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0080] The calcium aluminate may be formed by reaction of at least one calcium precursor and at least one of alumina, aluminum hydroxide and aluminum oxide hydroxide in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form calcium aluminate. Reaction conditions sufficient to form calcium aluminate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0081] The calcium zirconate may be formed by reaction of at least one calcium precursor and zirconia in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form calcium zirconate. Reaction conditions sufficient to form calcium zirconate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0082] The magnesium titanate may be formed by reaction of at least one magnesium precursor and TiO₂ in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form magnesium titanate. Reaction conditions sufficient to form magnesium titanate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0083] The magnesium aluminate may be formed by reaction of at least one magnesium precursor and at least one of alumina, aluminum hydroxide and aluminum oxide hydroxide in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form magnesium aluminate. Reaction conditions sufficient to form magnesium aluminate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0084] The magnesium zirconate may be formed by reaction of at least one magnesium precursor and zirconia in a mixture with at least one of calcium carbonate and magnesium carbonate under reaction conditions sufficient to form magnesium zirconate. Reaction conditions sufficient to form magnesium zirconate may include a temperature range of 600°C to 1050°C and a pressure range of 0.1 atm to 100 atm (0.1 to 100 bar).

[0085] Aggregates suitable for carbon dioxide sorption may be made by a method of making an aggregate comprising (a) preparing a mixture comprising water, at least one of calcium carbonate and magnesium carbonate, at least one of a calcium precursor and a magnesium precursor, at least one of Al(OH)₃, AlO(OH), Al₂O₃, TiO₂, and ZrO₂, and optionally a pore former; (b) forming a green aggregate from the mixture; (c) heating the green aggregate; (d) maintaining the green aggregate within a temperature range for a first time period; (e) heating the green aggregate further; (f) maintaining the green aggregate within another temperature range for a second time period; and (g) cooling the green aggregate to make the aggregate. The green aggregate is exposed to an atmosphere comprising oxygen during at least one of the steps (a) through (f). The green aggregate may be exposed to an atmosphere comprising oxygen during all of the steps (a) through (f). The atmosphere comprising oxygen may be air.

[0086] As used herein, "green" means not fully processed or fully treated.

[0087] In the step of preparing the mixture, the mixture comprises calcium carbonate, magnesium carbonate or a mixture of calcium carbonate and magnesium carbonate in an amount to provide 15 to 75 mass % or 15 to 65 mass % of the calcium oxide, magnesium oxide or mixture of calcium oxide and magnesium oxide in the aggregate. The mixture also comprises at least one of a calcium precursor and a magnesium precursor in an amount to provide 25 to 85 mass % or 35 to 85 mass % of the binding agent in the aggregate. The mixture also comprises at least one of TiO₂, Al₂O₃, ZrO₂, Al(OH)₃ and AlO(OH) in an amount to provide 25 to 85 mass % or 35 to 85 mass % of the binding agent, which is formed in-situ in the aggregate. The mixture also comprises 20 to 40 mass % water for making pellets and 20 to 80 mass % water for making granules. One skilled in the art can calculate the amount of starting material to form the desired concentration of constituents in the final aggregate.

[0088] The calcium carbonate and/or magnesium carbonate may have a particle size between 0.1 and 74 microns or between 0.1 and 44 microns. Calcium carbonate, magnesium carbonate and mixtures of calcium carbonate and magnesium carbonate are commercially available. They can also be synthesized by precipitating them from water soluble salts of calcium and/or magnesium.

[0089] The amount of calcium carbonate and/or magnesium carbonate used in the mixture may be adjusted to provide the amount of free calcium oxide and/or mag-

nesium oxide desired in the aggregate for CO₂ sorption and desorption. The calcium carbonate and/or magnesium carbonate decomposes during the calcinations, producing pores in the aggregate due to the release of CO₂. Calcium precursor and/or magnesium precursor (e.g. calcium oxide and/or magnesium oxide) used in the mixture is provided in an amount sufficient to react with the TiO₂, Al₂O₃, ZrO₂, Al(OH)₃ and/or AlO(OH) during calcinations and form an amount of the respective binding agent in-situ and effective to provide strength and hold the particles together.

[0090] The TiO₂ may be in Anatase form. Alumina may be in the form of gamma alumina. Aluminum hydroxide may be in the form of boehmite. The TiO₂, alumina, zirconia and aluminum hydroxide may have particle sizes between 0 and 10 microns.

[0091] The calcium precursor used for forming calcium titanate, calcium aluminate or calcium zirconate may be selected from CaO, Ca(OH)₂, CaCO₃, Ca(NO₃)₂ and Ca(CH₃CO₂)₂. The calcium precursor may have a particle size between 0.1 and 10 microns.

[0092] The magnesium precursor used for forming magnesium titanate, magnesium aluminate or magnesium zirconate may be selected from MgO, Mg(OH)₂, MgCO₃, Mg(NO₃)₂ and Mg(CH₃CO₂)₂. The magnesium precursor may have a particle size between 0 and 10 microns.

[0093] The mixture may optionally further comprise 0.1 to 5 mass % or 1 to 3 mass % of a pore former. The pore former may be methocel pore former or other pore former known in the art. Suitability of various pore former may be determined without undue experimentation. The use of an optional pore former permits further adjustment of internal porosity.

[0094] The mixture may optionally further comprise 0.1 to 10 mass % or 0.2 to 5 mass % of at least one metal selected from Ni, Pt, Rh, and Pd.

[0095] In the step of forming the aggregate where the aggregate is a pellet, the pellet may be formed by extruding the mixture through a die thereby forming an extrudate-type pellet. Alternatively, the pellet may be formed by compressing the mixture in a mold. Any method of forming a pellet known in the art may be used.

[0096] The aggregate may be optionally dried for 6 to 24 hours in air. The aggregate may be optionally dried in an oven at 105°C to 125°C for 6 to 24 hours in air.

[0097] In the step of forming granular material, the granular material may be formed from the slurry by spray drying or any other method of forming granular material known in the art.

[0098] In the step of forming the aggregate where the aggregate is a granule, the granules may be formed by spray drying or other technique known in the art.

[0099] In the step of heating the green aggregate, the green aggregate is heated from a first temperature, T_1 , to a second temperature, T_2 , at a first average heating rate between 0.1°C/minute to 10°C/minute. The first temperature T_1 , is within a first temperature range, wherein

the first temperature range is between 5°C and 50°C. The first temperature may be room temperature (about 25°C). The second temperature T_2 , is a minimum temperature, T_{2min} , of a second temperature range, the second temperature range extending from the minimum temperature, T_{2min} , of the second temperature range to a maximum temperature, T_{2max} , of the second temperature range. The minimum temperature, T_{2min} , of the second temperature range may be 600°C or 650°C and the maximum temperature, T_{2max} , of the second temperature range may be 700°C or 750°C.

[0100] In the step of heating the green aggregate, the time to heat from the first temperature to the second temperature is the first heating time, t_1 . The first average

heating rate is defined as $\frac{T_2 - T_1}{t_1}$.

[0101] In the step of maintaining the green aggregate within a temperature range for a first time period, the green aggregate is maintained within the second temperature range and the first time period is between 15 minutes and 4 hours. When maintaining the temperature within the second temperature range, the temperature may be increased and/or decreased within the second temperature range.

[0102] In the step of heating the green aggregate further; the green aggregate is heated from the maximum temperature, T_{2max} , of the second temperature range to a third temperature, T_3 , at a second average rate of 0.1°C/minute to 10°C/minute, wherein the third temperature is a minimum temperature, T_{3min} , of a third temperature range, the third temperature range extending from the minimum temperature, T_{3min} , of the third temperature range to a maximum temperature, T_{3max} , of the third temperature range wherein the minimum temperature, T_{3min} , of the third temperature range is 900°C and the maximum temperature, T_{3max} , of the third temperature range is 1050°C.

[0103] In the step of heating the green aggregate further, the time to heat from the maximum temperature, T_{2max} , of the second temperature range to the third temperature, T_3 , is the second heating time, t_2 . The second

average rate is defined as $\frac{T_3 - T_{2max}}{t_2}$.

[0104] In the step of maintaining the green aggregate within another temperature range for a second time period, the aggregate is maintained within the third temperature range and the second time period is between 15 minutes and 4 hours. When maintaining the temperature within the third temperature range, the temperature may be increased and/or decreased within the third temperature range.

[0105] In the step of cooling the green aggregate, the aggregate is cooled to a fourth temperature, T_4 , wherein the fourth temperature is within a fourth temperature

range. The fourth temperature range is between 0°C and 50°C. The fourth temperature may be, for example, room temperature. Cooling may be by one or more of natural convection, forced convection, conduction and radiation. The rate or method of cooling is not critical.

[0106] The apparatus for producing a CO₂-depleted gas from a CO₂-containing gas comprises a bed containing a plurality of the described aggregates. The bed may be a fixed bed, ebullated bed, expanded bed, moving bed or fluidized bed type apparatus. The various types of beds are well-known in the art.

[0107] The apparatus can be constructed by one skilled in the art. Suitable materials of construction are known in the art for the process conditions. The apparatus may be insulated if desired and may be operated adiabatically if desired.

[0108] A CO₂-depleted gas is any gas formed from a CO₂-containing gas and having a CO₂ concentration less than the CO₂-containing gas. A CO₂-containing gas is any gas containing CO₂.

[0109] The CO₂-containing gas may be a flue gas (i.e. combustion products from a furnace, boiler or the like), or other CO₂-containing gas stream. Sulfur-containing gases may be removed from the CO₂-containing stream prior to removing CO₂.

[0110] The process for producing a CO₂-depleted gas from a CO₂-containing gas comprises:

(i) passing the CO₂-containing gas through a bed containing a plurality of the described aggregates under conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate with the plurality of aggregates and withdrawing the CO₂-depleted gas;

(ii) regenerating the bed by passing a purge gas through the bed under conditions sufficient to liberate CO₂ from the plurality of aggregates and withdrawing a by-product gas comprising CO₂ from the reactor; and

(iii) repeating (i) and (ii) in a cyclic manner.

[0111] The conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate may include a temperature ranging from 600°C to 800°C, preferably 650°C to 800°C, and a pressure ranging from 1 to 100 atmospheres (1 to 100 bar).

[0112] The conditions sufficient to liberate CO₂ may include a temperature ranging 650°C to 900°C and a pressure ranging from 0.9 to 100 atmospheres (0.9 to 100 bar) or a pressure ranging from 0.9 to 2 atmospheres (0.9 to 2 bar).

[0113] The CO₂ removal may be characterized by a sorption temperature and the regeneration step may be characterized by a regeneration temperature, wherein the regeneration temperature may be greater than the sorption temperature and wherein the difference be-

tween the regeneration temperature and the sorption temperature may be 200°C or less.

[0114] The purge gas may comprise oxygen, nitrogen and/or steam. The purge gas may comprise at least one of nitrogen and steam and may optionally comprise oxygen. The purge gas may be air or steam.

[0115] The process will be illustrated with reference to FIG. 1.

[0116] A process flow diagram for an apparatus 101 for producing a CO₂-depleted gas from a CO₂-containing gas is shown in FIG. 1.

[0117] A CO₂-containing gas stream 110 is introduced into bed 130 by way of valve 112. Valve 124 is closed. The CO₂-containing gas is passed into bed 130, which contains the CO₂ sorbing aggregates described herein. The CO₂-containing gas is passed through the bed 130 under conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate and thereby form CO₂-depleted gas 150 which is withdrawn via valve 132. Valve 134 is closed.

[0118] After a time, which depends on the size of the bed 130, the bed will become substantially saturated with CO₂ and will need to be regenerated. Valve 112 and valve 132 are closed and a purge gas 160 is passed via valve 134 through the bed 130 to liberate the CO₂ from the aggregates. A by-product gas 120 comprising CO₂ is withdrawn from the bed 130 via valve 124.

[0119] During the time that bed 130 is undergoing the regeneration step, bed 140 is forming the CO₂-depleted gas 150. The CO₂-containing gas stream 110 is introduced into bed 140 by way of valve 114. Valve 122 is closed. The CO₂-containing gas is passed into bed 140, which contains the CO₂ sorbing aggregates described herein. The CO₂-containing gas is passed through the bed 140 under conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate and thereby form CO₂-depleted gas 150 which is withdrawn via valve 142. Valve 144 is closed.

[0120] During the time that bed 130 is producing the CO₂-depleted gas, bed 140 is regenerating. Valve 114 and valve 142 are closed and purge gas 160 is passed via valve 144 through bed 140 to liberate the CO₂ from the pellets in bed 140. By-product gas 120 comprising CO₂ is withdrawn from bed 140 via valve 122.

[0121] The beds operate cyclically.

[0122] While described as a process and apparatus using two beds, any suitable number of beds may be used.

[0123] The purge gas may be introduced into the beds from the same end (co-current) or from the opposite end (counter-current) as the process gas

[0124] When the beds are fixed beds, the aggregates are preferably pellets.

[0125] When the beds are one of ebullated, expanded, moving or fluidized beds, the aggregates are preferably granules.

[0126] In another aspect, the present invention relates to a reactor and a process for producing a hydrogen-

containing gas by the reaction of one or more gaseous hydrocarbons with gaseous water, i.e. steam, under reaction conditions effective to form hydrogen.

[0127] The reactor for producing a hydrogen-containing gas comprises a bed containing CO₂-sorptive aggregates. The bed optionally contains steam-hydrocarbon reforming catalyst aggregates comprising a reforming catalyst, and optionally contains metal oxides of at least one of Cu, Fe and Ni. The purpose of the optional metal oxides is to promote the reforming reaction and to provide a source of oxygen during hydrogen production.

[0128] The reactor may be a fixed-bed reactor. The fixed-bed reactor may be a tubular reactor. The reactor may be an ebullated, expanded, fluidized bed, or moving bed reactor. The various reactor types are well-known in the art.

[0129] In order to carry out the steam-hydrocarbon reforming reaction, at least a portion of the CO₂-sorptive aggregates may comprise a catalyst material suitable for steam-hydrocarbon reforming and/or separate steam-hydrocarbon reforming catalyst aggregate (e.g. pellets or granules) and/or metal oxides of at least one of Cu, Fe and Ni may be contained in the bed. If desired, the bed may additionally contain other types of pellets or granules, flow directing devices, or the like.

[0130] At least a portion of the CO₂-sorptive aggregates comprise at least one metal selected from Ni, Pt, Rh and Pd when the bed does not contain steam-hydrocarbon reforming catalyst aggregates or metal oxides of at least one of Cu, Fe and Ni or other material capable of promoting the reforming reaction. Ni, Pt, Rh and/or Pd act as a catalyst for the steam-methane reforming reaction. The CO₂-sorptive aggregates may optionally comprise Ni, Pt, Rh and Pd when the bed does contain steam-hydrocarbon reforming catalyst aggregates or metal oxides capable of promoting the reforming reaction.

[0131] When at least one metal is included, the CO₂-sorptive aggregates may comprise 0.1 to 10 mass % or 0.2 to 5 mass % of at least one metal selected from Ni, Pt, Rh, and Pd.

[0132] When both CO₂-sorptive pellets and steam-hydrocarbon reforming catalyst pellets are used, it is preferred to have the pellet types distributed more or less evenly throughout the bed.

[0133] When CO₂-sorptive pellets, steam-hydrocarbon reforming catalyst pellets and metal oxide pellets are used, it is preferred to have the pellet types distributed more or less evenly throughout the bed.

[0134] When both CO₂-sorptive granules and steam-hydrocarbon reforming catalyst granules are used, it is preferred to have the granule types distributed more or less evenly throughout the bed.

[0135] When CO₂-sorptive granules, steam-hydrocarbon reforming catalyst granules and metal oxide granules are used, it is preferred to have the granule types distributed more or less evenly throughout the bed.

[0136] Suitable steam-hydrocarbon reforming catalyst pellets are known in the art and are available commer-

cially. Suitable steam-hydrocarbon reforming process catalysts include any materials effective for the reforming of methane or higher hydrocarbons with steam to produce hydrogen. These materials may include, for example, any of nickel, cobalt, the platinum group metals (i.e. ruthenium, osmium, rhodium, palladium, platinum, and iridium) and oxides of the foregoing metals. The materials may be supported on zirconia, alumina, or other suitable supports known in the art.

[0137] Suitable steam-hydrocarbon reforming catalyst in granular form can be purchased from a commercial vendor or prepared by crushing and/or grinding the pelleted catalyst.

[0138] Suitable steam-hydrocarbon reforming catalyst for providing oxygen during the reforming reaction may include oxides of metals of at least one of Ni, Fe and Cu. These metals may be unsupported or supported, for example supported on zirconia, alumina, or other suitable supports known in the art.

[0139] A reactor comprising a bed of CO₂-sorptive aggregates and optionally containing steam-hydrocarbon reforming catalyst aggregates and/or metal oxides can be constructed by one skilled in the art of hydrogen production.

[0140] Suitable materials for the operating conditions are known. The construction of reactors for the production of hydrogen is known in the art.

[0141] The reactor may be insulated if desired. The reactor may be operated as an adiabatic reactor.

[0142] The process for producing a hydrogen-containing gas comprises reacting methane with steam in a bed of CO₂-sorptive aggregates in a production step under reaction conditions sufficient to form hydrogen gas and metal carbonate from calcium oxide and/or magnesium oxide-containing aggregates. At least a portion of the calcium oxide and/or magnesium oxide-containing aggregates may comprise a catalyst material suitable for steam-hydrocarbon reforming and/or separate steam-hydrocarbon reforming catalyst aggregates may be contained in the bed and/or separate metal oxides of at least one of Cu, Fe and Ni may be contained in the bed as described above in the description of the reactor.

[0143] The discussion above relating to the CO₂-sorptive aggregates and the steam-hydrocarbon reforming catalyst aggregates applies also to the method.

[0144] Typically, the bed is maintained at an elevated temperature, and the reforming reactions may be effected in the range of 350°C to 900°C and more specifically in the range of 600°C to 800°C. The pressure in the reactor may range from 1 to 100 atmospheres (1 to 100 bar). These temperatures and pressures are suitable reaction conditions sufficient to form hydrogen and carbonate from the calcium oxide and/or magnesium oxide-containing aggregates. Preferred reaction conditions for forming hydrogen and reduced calcium oxide and/or magnesium oxide-containing aggregates may be determined without undue experimentation.

[0145] The production step comprises introducing

steam and a feed gas containing methane into the reactor, reacting the methane with the steam in the bed in the presence of at least one of the reforming catalyst, the metal oxides of at least one of Cu, Fe and Ni, and the at least one metal selected from Ni, Pt, Rh and Pd under reaction conditions sufficient to form hydrogen and to form calcium carbonate and/or magnesium carbonate from CO₂-sorptive aggregates, and withdrawing a product gas comprising hydrogen (i.e. the hydrogen-containing gas) from the reactor.

[0146] The bed may comprise: (a) CO₂-sorptive aggregates comprising a reforming catalyst, (b) a supported or unsupported metal oxide of at least one of Cu, Fe and Ni; and CO₂-sorptive aggregates comprising a reforming catalyst, (c) a supported or unsupported metal oxide of at least one of Cu, Fe and Ni; steam-hydrocarbon reforming catalyst aggregates; and CO₂-sorptive aggregates comprising a reforming catalyst, (d) steam-hydrocarbon reforming catalyst aggregates and CO₂-sorptive aggregates not comprising steam reforming catalyst, and (e) a supported or unsupported metal oxide of at least one of Cu, Fe, and Ni; steam-hydrocarbon reforming catalyst aggregates, and CO₂-sorptive aggregates not comprising steam reforming catalyst.

[0147] In one or more embodiments, the bed contains the CO₂-sorptive aggregates and steam-hydrocarbon reforming catalyst aggregates comprising a reforming catalyst where the CO₂-sorptive aggregates include Ni, Pt, Rh or Pd. In these one or more embodiments, the production step comprises introducing steam and a feed gas containing methane into the reactor, reacting the methane and the steam in the bed in the presence of the reforming catalyst under reaction conditions sufficient to form hydrogen and calcium carbonate and/or magnesium carbonate from the CO₂-sorptive aggregates, and withdrawing a product gas comprising hydrogen (i.e. the hydrogen-containing gas) from the reactor.

[0148] In one or more embodiments, the bed contains the CO₂-sorptive aggregates and a metal oxide of at least one of Cu, Fe and Ni where the CO₂-sorptive aggregates do not include Ni, Pt, Rh or Pd. In these one or more embodiments, the production step comprises introducing steam and a feed gas containing methane into the reactor, reacting the methane and the steam in the bed in the presence of the metal oxides under reaction conditions sufficient to form hydrogen and calcium carbonate and/or magnesium carbonate from the CO₂-sorptive aggregates, and withdrawing a product gas comprising hydrogen (i.e. the hydrogen-containing gas) from the reactor.

[0149] In one or more embodiments, the bed contains the CO₂-sorptive aggregates where the CO₂-sorptive aggregates include at least one metal selected from Ni, Pt, Rh or Pd. In these one or more embodiments, the production step comprises introducing steam and a feed gas containing methane into the reactor, reacting the methane and the steam in the bed in the presence of the at least one metal under reaction conditions sufficient to form hydrogen and calcium carbonate and/or magnesi-

um carbonate from the CO₂-sorptive aggregates, and withdrawing a product gas comprising hydrogen (i.e. the hydrogen-containing gas) from the reactor.

[0150] Any hydrocarbons may be used which are capable of catalyzed reaction with steam to form hydrogen. The at least one hydrocarbon may be selected from aliphatic hydrocarbons having from 1 to 20 carbon atoms, and advantageously may be selected from aliphatic hydrocarbons having 1 to 6 carbon atoms. Desirably, the feed gas may be selected from methane, natural gas, propane, or a mixture of predominantly C₁ to C₄ aliphatic hydrocarbons.

[0151] The steam and the at least one hydrocarbon may be introduced as a gaseous feed mixture. A desirable gaseous feed mixture comprises steam and methane. The methane in the steam/methane gaseous mixture may be obtained from any suitable source, and may be, for example, natural gas from which sulfur compounds have been removed. It is advantageous to include a low level of hydrogen, e.g. about 3 mole % as a product recycle to an inlet to the reactor in order to assist in the reduction/activation of the catalyst and possibly to reduce the likelihood of carbon deposition, particularly where unreformed natural gas or C₂ and higher hydrocarbons are present in the feed.

[0152] The molar ratio of steam to carbon typically ranges from 1:1 to 4:1 or from 1.3:1 to 2.5:1. The steam to carbon ratio is a common parameter used in the field of hydrocarbon reforming.

[0153] The gaseous feed mixture may be a mixture of adiabatically pre-reformed hydrocarbon feedstock (e.g. natural gas) and steam. The adiabatic pre-reforming process is affected by heating the hydrocarbon feedstock to a temperature of about 500°C and passing the heated gas through an adiabatic nickel catalyst bed. Natural gas typically contains about 5% of heavy hydrocarbon fractions, wherein the term "heavy" is understood to mean fractions containing two or more carbon atoms. The heavy fractions are typically more reactive than methane, and catalytically reform to yield carbon dioxide and hydrogen. The resulting gas mixture therefore contains a mixture of methane, carbon dioxide, steam and hydrogen. The pre-reforming reactions typically are endothermic, and because the reaction usually precedes adiabatically, the temperature of the resulting gas mixture decreases. Typically, the temperature of the gas mixture is reduced to about 450°C after pre-reforming.

[0154] The use of pre-reformed natural gas instead of untreated natural gas has associated advantages. First, the pre-reforming process generates some hydrogen, which is useful for chemically reducing to an active state the catalyst for the subsequent steam-methane reforming reaction. Second, the removal of the heavy hydrocarbon fractions reduces the potential for carbon deposition on the steam-methane reforming catalyst. The use of pre-reforming extends the life of the catalyst, since carbon deposition ultimately leads to the deactivation of the catalyst.

[0155] The regeneration step comprises regenerating the reactor by heating the CO₂ saturated CO₂ sorptive aggregates under the flow of a purge gas under reaction conditions sufficient to liberate CO₂. The purge gas may comprise at least one of nitrogen and steam and may optionally comprise oxygen. The purge gas may be air or steam. The regeneration pressure may be 0.9 to 100 atmospheres (0.9 to 100 bar) or 0.9 to 2 atmospheres (0.9 to 2 bar). The regeneration step may be characterized by a regeneration temperature in the range of 450°C to 900°C.

[0156] In another embodiment, the regeneration step comprises regenerating the reactor by heating the CO₂ saturated CO₂-sorptive aggregates under the flow of a purge gas under reaction conditions sufficient to liberate CO₂ and oxidize the reduced metal oxides. The purge gas comprises oxygen and optionally comprises at least one of nitrogen and steam. The regeneration pressure may be 0.9 to 100 atmospheres (0.9 to 100 bar) or 0.9 to 2 atmospheres (0.9 to 2 bar). The regeneration step may be characterized by a regeneration temperature in the range of 450°C to 900°C.

[0157] The production step may be characterized by a production temperature and the regeneration step may be characterized by a regeneration temperature, wherein the regeneration temperature may be greater than the production temperature and wherein the difference between the regeneration temperature and the production temperature may be 100°C or less.

[0158] The product gas comprising hydrogen may be further processed and purified by pressure swing adsorption or other suitable means if desired.

[0159] The generation of hydrogen from hydrocarbons and steam using the method, process and reactor may be illustrated by way of exemplary process flowsheet of the FIG. 2.

[0160] A hydrocarbon-containing feed gas, for example, methane provided by natural gas, optionally mixed with 1-15 mole% hydrogen, flows via conduit 1 at a pressure in the range of 100 to 600 psia (690 to 4100 kPa) to preheat exchanger 3 and is heated therein to a typical temperature in the range of 200°C to 400°C by heat exchange with a hot process stream (later defined) supplied via conduit 5. The feed may be desulfurized using metal promoted carbon (not shown) prior to conduit 1, or using ZnO (not shown) after preheating but prior to conduit 7. The heated feed flows via conduit 7 and open valve 9 and is mixed with process steam provided via conduit 11 to form a hydrocarbon-steam feed mixture. Alternatively, steam may be added prior to valve 9 if desired (not shown).

[0161] The steam-hydrocarbon mixture is introduced into heat exchange zone 13 and is further heated therein by heat exchange with a hot process stream (later defined). The heat exchange zone described here can be a recuperative or a conventional heat exchanger. Heat exchange can take place against any of the hot streams exiting the reactor. The steam-hydrocarbon mixture may

be heated to a temperature in the range of 350°C to 900°C, and typically may be in the range of 600°C to 800°C. The heated mixture then is introduced via conduit 16 into reactor 17, which has a bed packed with CO₂ sorptive-containing pellets and optionally steam-hydrocarbon reforming catalyst as discussed for the method, process and reactor. Alternatively, the heat exchange zone can be a portion of the reactor itself, at either or both of its ends, and conduits may not be necessary. The reactor 17 itself may be substantially adiabatic and insulated, preferably by an internal lining of refractory material (s). The feed mixture reacts in the bed to form primarily hydrogen and carbon dioxide, and, in much smaller amounts, carbon monoxide. The carbon dioxide is substantially retained by reaction with the CO₂ sorptive pellets in the bed.

[0162] The reaction product effluent stream flows via conduit 15 to heat exchange zone 13, where it is cooled to a temperature in the range of 250°C to 500°C by heat exchange with incoming reactants as earlier described, or regenerate as described below. The cooled reaction product effluent stream exits heat exchange zone 13 via open valve 21 and is further cooled in heat exchange zone 3 and optionally boiler 23 to yield a further cooled reaction product effluent stream in conduit 25 at a typical temperature of 40°C. Any condensate is knocked out at this point (not shown).

[0163] The cooled reaction product stream containing hydrogen, small amounts of carbon dioxide, carbon monoxide and unreacted methane is introduced into pressure swing adsorption (PSA) system 27 and is separated therein to yield a high-purity hydrogen product containing at least 99 vol. % hydrogen that is withdrawn via conduit 29. Components removed from the hydrogen by the PSA system typically include carbon dioxide, water, methane and carbon monoxide, and these are withdrawn in a waste gas via conduit 31 during the blowdown and purge steps typically used in PSA process cycles. Any PSA cycle and system known in the art may be used in the process described in this and other embodiments of the invention. The waste gas in conduit 31 typically contains combustible components and may be used as fuel in a fired boiler, 33, or in a direct fired heater to preheat regenerant air (not shown).

[0164] The mixture of CO₂ sorptive pellets and steam-hydrocarbon reforming catalyst in reactor 17 has a finite capacity for carbon dioxide. Once this is exhausted, the purity and yield of hydrogen in the reaction product effluent stream leaving reactor 17 via conduit 19 will begin to decrease. The time at which this occurs can be determined by real-time analysis of the stream by any known analytical means, such as, for example, in-line IR spectroscopy. At this point, reactor 17 is switched to regeneration mode by closing valve 9 and depressurizing the reactor via conduits 19, conduit 32, conduit 35, open valve 37, and conduit 39, wherein the hydrocarbon-containing blowdown gas is introduced into boiler 33 or a direct fired air heater (not shown). At this point, valve 41

remains closed. The blowdown can be cocurrent or countercurrent. In case the blowdown is countercurrent, the piping would need to be modified accordingly.

[0165] Valve **37** is then closed, valve **41** is then opened and reactor **17** may be purged with a suitable purge gas such as steam or nitrogen to remove residual hydrocarbons from the reactor void volume. In this embodiment, steam for purge is provided via conduit **11** and flows through heat exchanger **13** and conduit **16** into the reactor. Purge effluent gas leaves the reactor via conduits **19** and **32**, flows through heat exchanger **43**, open valve **41**, conduit **45**, heat exchanger **47**, and conduit **49** into boiler **33**. The purge may be cocurrent or countercurrent with appropriate modifications to the flowsheet, easily recognized by one skilled in the art.

[0166] A particular feature of this embodiment is that the switching valves such as valve **9** or **51** are on the cooler side of the heat exchange zones **13** or **43**. While this requires each reactor to be associated with its individual heat exchange zone, it does ease the mechanical requirements and operating life of the switching valves. It is possible to combine heat exchange zones **13** and **43** into a single heat exchanger (not shown here), but that would require the valves to be repositioned to the hotter side of the heat exchange zone.

[0167] The figure shows the heat exchange zones to be of the conventional type where heat exchange between streams is contemporaneous. The heat exchange zones could also be recuperative in nature (not shown), where heat from a cooling stream is stored in the heat capacitance of the zone, and released to a warming stream in a subsequent step. The zones would comprise of inert solids such as ceramic pellets or firebrick. They could be located in a separate vessel, or form a portion of the reactor vessel itself at either or both ends, adjacent to the reaction zone which is the active zone filled with CO₂ sorptive pellets and reforming catalyst.

[0168] Regeneration of reactor **17** then is initiated by opening previously-closed valve **51**. A regeneration gas selected from air, steam, nitrogen or a mixture thereof is provided via intake conduit **55** to compressor **57** and is compressed therein to 15 to 100 psia (690 kPa) and the compressed regeneration gas in conduit **59** is preheated in heat exchanger **47** to 250°C to 500°C, and introduced via conduit **61** and valve **51** into the heat exchange zone **43**. The regeneration gas is further heated in heat exchange zone **43** against hot exhaust gas from conduit **32** (later described), or hot reactor effluent as described earlier, to a temperature between 500°C and 900°C, typically from 700°C to 800°C. The heated regenerated gas flows via conduits **53** and **16** into reactor **17**, and the heated regeneration gas regenerates CO₂ sorptive pellet by releasing the carbon dioxide previously reacted with the CO₂ sorptive pellet material. The carbon dioxide-rich regeneration off-gas leaves the reactor via conduit **19** and conduit **32** at a temperature in the range of 600°C to 900°C and typically from 650°C to 800°C. The hot regeneration off-gas in conduit **32** is introduced into heat

exchange zone **43** (this may be integrated with heat exchange zone **13**) to heat the regeneration gas entering via valve **51** as earlier described, or to heat the hydrocarbon-steam feed mixture as earlier described, whereby the off-gas is cooled to a temperature in the range of 350°C to 600°C. The cooled regeneration off-gas flows via valve **41** and is further cooled to a temperature in the range of 200°C to 30°C in heat exchanger **47**, thereby heating compressed air stream **59** as earlier described. The cooled regeneration off-gas stream in conduit **49** may be introduced into boiler **33** for additional heat recovery.

[0169] Following the substantial regeneration of reactor **17** by removal of most or all of the carbon dioxide retained therein during the reaction step, the reactor may be purged with an inert gas and repressurized with steam, feed gas, or product gas. Following repressurization, the reactor proceeds to the reaction step and the cycle is repeated as described earlier.

[0170] Reactor **63** is operated through the same cycle steps described above for reactor **17**, but the cycle of reactor **63** is staggered so that it operates in the regeneration mode when reactor **17** operates in the reaction or hydrogen production mode. Hydrocarbon-containing feed gas flows via valve **65**, steam is added via conduit **67**, the feed-steam mixture is heated in heat exchanger **13**, and the heated feed flows via conduits **69** and **71** to reactor **63**. Reaction product gas leaves the reactor via conduits **72** and **73**, is cooled in heat exchanger **13**, and flows via valve **75**, conduit **5**, heat exchanger **3**, boiler **23**, and conduit **25** to PSA system **27**. Regeneration gas is provided to reactor **63** via valve **77**, heat exchanger **43**, and conduit **71**, and blowdown or depressurization gas exits via conduit **81**, valve **83**, and conduit **39** into boiler **33**. Regeneration off-gas leaves reactor **63** via conduit **85**, heat exchanger **43**, and valve **87**, and then flows via conduit **45**, heat exchanger **47**, and conduit **49** to boiler **33**.

[0171] Reactors **17** and **63** thus are operated in a staggered sequence between the hydrogen production and regeneration modes by the proper operation of switch valves **9**, **21**, **37**, **41**, **51**, **65**, **75**, **77**, **83**, and **87** as described above. Operation with two parallel reactors with constant hydrogen product flow is possible when the elapsed time of the hydrogen production mode is equal to or greater than that of the regeneration mode. However, any suitable number of reactors in parallel may be used in staggered operation to achieve continuous hydrogen production. In practice, the duration of the hydrogen production step may be different than the duration of the regeneration step. For example, if the regeneration step is twice as long as the production step, a configuration employing three parallel beds may be advantageously used wherein two beds are being regenerated while the third bed is used for hydrogen production.

Examples

[0172] Several batches of pellets were made from calcium oxide, calcium carbonate, and a mixture of calcium oxide and calcium carbonate using a wide variety of techniques described below in the examples. The strength of these particulate were determined by crushing them and determining the force per unit length required to crush the pellet. The diameter of pellet was determined by measuring it by a caliper.

[0173] The CO₂ sorption/desorption performance of calcium oxide-containing pellets was determined by using a thermogravimetric analyzer (TGA). A sample was placed in the TGA apparatus and heated to 700°C or 750°C while purging with an inert nitrogen gas stream. The sample was then exposed to a humidified gas containing CO₂ for 15 min to chemically sorb carbon dioxide from the gas mixture, thereby forming CaCO₃. The gain in weight due to sorption of CO₂ by calcium oxide pellets was recorded by the TGA instrument. The calcium oxide pellets saturated with CO₂ and heated to 700°C or 750°C was regenerated by exposing it to air for 15 minutes. The exposure to air decomposed CaCO₃ and reproduced calcium oxide. The weight loss due to CO₂ removal from the calcium oxide pellets was recorded again by the TGA instrument. The cycling between exposing calcium oxide pellets to a gas containing CO₂ and air was repeated for a specified number of cycles as detailed in each example.

Example 1

[0174] In example 1, CaO-calcium aluminate pellets were prepared according to conventional techniques. A mixture was prepared by mixing 69.7g of calcium oxide (prepared by decomposing calcium carbonate at 900°C), 40g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaO and alumina in the mixture was sufficient to (a) stoichiometrically produce a nominal composition of 3CaO·2Al₂O₃ and (b) provide sufficient amount of CaO to produce CaO-calcium aluminate containing 45 wt% of free CaO. The particle size of CaO and alumina powders was about 10 microns. Approximately 82g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in

final form.

[0175] XRD analysis of the fresh pellets identified CaO as the major phase, Ca₃Al₂O₆ as a low major phase and a trace of Ca₁₂Al₁₄O₃₃.

[0176] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 1049 angstroms (104.9 nm) and the porosity was 40.8 %.

[0177] The pellets were tested by exposing them to 50 cycles of the CO₂ sorption/desorption cycle test in the TGA using a humidified atmosphere described above for the CO₂ sorption/desorption cycle test. Both the sorption and desorption was carried out at 750°C. These pellets showed an initial CO₂ sorption capacity of 15 mass %.

The CO₂ sorption capacity of the pellets decreased continuously with the number of cycles. The CO₂ sorption capacity of pellets after 50 cycles was 8 mass%. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength (defined as the force needed crush a pellet on its side divided by its length) of the pellets increased from 3.5 lbf/mm (15.6 N/mm) initially to 4.9 lbf/mm (21.8 N/mm) after 50 cycles.

[0178] The pellets made according to example 1 exhibited strength and dimensionally stability. However, the CO₂ sorption capacity decreased after only 50 sorption/desorption cycles.

Example 2

[0179] In example 2, CaO-calcium aluminate pellets were prepared according to conventional techniques. A mixture was prepared by mixing 67.5g of calcium oxide (prepared by decomposing calcium carbonate at 900°C), 25g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaO and alumina in the mixture was sufficient to (a) stoichiometrically produce a nominal composition of 3CaO·2Al₂O₃ and (b) provide sufficient amount of CaO to produce CaO-calcium aluminate containing 60 wt% of free CaO. The particle size of CaO and alumina powders was about 10 microns. Approximately 81 g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in final form.

[0180] XRD analysis of the fresh pellets identified CaO and $\text{Ca}_3\text{Al}_2\text{O}_6$ as major phases with $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ as a low minor phase.

[0181] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 930 angstroms (93 nm) and the porosity was 47.1 %.

[0182] The pellets were tested by exposing them to 50 cycles of CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 23 mass %. The CO_2 sorption capacity of the pellets decreased continuously with the number of cycles. The CO_2 sorption capacity of pellets after 50 cycles was 13 mass%

Example 3

[0183] In example 3, CaO-calcium aluminate pellets were prepared in accordance with the present invention. A mixture was prepared by mixing 77.5g of calcium carbonate, 23.8g of CaO (prepared by decomposing calcium carbonate at 900°C), and 40g of alumina in the form of boehmite (75% pure alumina). The amount of CaO and alumina in the mixture was sufficient to stoichiometrically produce a nominal composition of $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$. In addition, the amount of calcium carbonate, CaO, and alumina in the mixture was sufficient to produce CaO-calcium aluminate containing 44 wt% of free CaO. The particle size of calcium carbonate, CaO and alumina powders was about 10 microns. Approximately 58g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. The pellets were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in final form.

[0184] XRD Analysis of the fresh sample identified a phase mixture of CaO, $\text{Ca}_2\text{Al}_2\text{O}_5$, $\text{Ca}_3\text{Al}_2\text{O}_6$, CaAl_2O_4 , and $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$.

[0185] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 9973 angstroms (997.3 nm) and the porosity was 49.4 %.

[0186] The pellets made in example 3 were tested in a variety of ways.

[0187] The pellets were tested by exposing them to 50 cycles of CO_2 sorption/desorption in the TGA using a

humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 23 mass %. The CO_2 sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.9 lbf/mm (8.4 N/mm) to 2.5 lbf/mm (11.1 N/mm) after 50 cycles.

[0188] The pellets were also tested by exposing them to 200 cycles of CO_2 sorption/desorption in the TGA using a humidified atmosphere as described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 27 mass %. The CO_2 sorption capacity of the pellets did not change even after 200 cycles. The diameter of pellets did not change after 200 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased to 2.4 lbf/mm (10.7 N/mm) after 200 cycles.

[0189] The pellets were also tested for 50 cycles of CO_2 sorption/desorption in a tubular reactor. The CO_2 sorption was carried out using a mixture containing 50% CO_2 and 50% steam. The CO_2 desorption was carried out by using 50% air and 50% steam. Both sorption and desorption were carried out at 750°C. After completing 50 sorption and desorption cycles in the tubular reactor, the pellets were removed from the tubular reactor. There was no change in the diameter of the pellets.

[0190] The pellets that were tested in the tubular reactor were tested again by exposing them to 50 cycles of the CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 27 mass %. The CO_2 sorption capacity of the pellets did not change even after 50 cycles in TGA. The diameter of pellets did not change after 50 sorption and desorption cycles in TGA. The final crush strength of the pellets after 50 cycles in the tubular reactor and 50 cycles in the TGA was 3.4 lbf/mm (15.1 N/mm).

[0191] Other pellets were tested for 50 cycles of CO_2 sorption/desorption in a tubular reactor for the CO_2 sorption/desorption cycle test. The CO_2 sorption was carried out using a mixture containing 50% CO_2 and 50% steam. The CO_2 desorption was carried out by using a mixture containing 50% air and 50% steam. Both sorption and desorption was carried out at 750°C. After completing 50 sorption and sorption cycles in the tubular reactor, the pellets were removed from the tubular reactor. There was no change in the diameter of the pellets.

[0192] The pellets that were tested in the tubular reactor were further tested by exposing them to 200 cycles of CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed a CO_2 sorption capacity of 24 mass % after 200 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles in TGA. The final crush strength

of the pellets after 50 cycles in the tubular reactor and 200 cycles in the TGA was 3.2 lbf/mm (14.2 N/mm).

[0193] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO₂ sorption capacity. These pellets can be made by the present method.

Example 4

[0194] In example 4, CaO-calcium aluminate pellets were made according to the present method. A mixture was prepared by mixing 90g of calcium carbonate, 15.1 g of CaO (prepared by decomposing calcium carbonate at 900°C), 25g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaO and alumina in the mixture was sufficient to stoichiometrically produce a nominal composition of 3CaO.2Al₂O₃. In addition, the amount of calcium carbonate, CaO, and alumina in the mixture was sufficient to produce CaO-calcium aluminate containing 59 wt% free CaO. The particle size of calcium carbonate, CaO and alumina powders was about 10 microns. Approximately 52g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in final form.

[0195] XRD analysis of the fresh sample identified the major phase was very strong CaO with minor Ca₃Al₂O₆ and low minor Ca₁₂Al₁₄O₃₃ and CaAl₂O₄.

[0196] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 15922 angstroms (1592.2 nm) and the porosity was 64 %.

[0197] The pellets were tested by exposing them to 50 cycles of CO₂ sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO₂ sorption capacity of 30 mass %. The CO₂ sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. The crush strength of the pellets increased from 1.8 lbf/mm (8.0 N/mm) to 2.2 lbf/mm (9.8 N/mm) after 50 cycles.

[0198] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO₂ sorption capacity. These pellets can be

made by the present method.

Example 5

[0199] In example 5, CaO-calcium aluminate pellets were prepared according to the present method. A mixture was prepared by mixing 100g of calcium carbonate, 10.3g of CaO (prepared by decomposing calcium carbonate at 900°C), 17.2g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaO and alumina in the mixture was sufficient to stoichiometrically produce a nominal composition of 3CaO.2Al₂O₃. In addition, the amount of calcium carbonate, CaO, and alumina in the mixture was sufficient to produce CaO-calcium aluminate containing 76 wt% free CaO. The particle size of calcium carbonate, CaO and alumina powders was about 10 microns. Approximately 48g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled down to room temperature to form the pellets in final form.

[0200] XRD analysis of the fresh sample identified - the major phase was very strong CaO, with minor Ca₃Al₂O₆ and CaAl₂O₄, and weak Ca₂Al₂O₅.

[0201] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 31891 angstroms (3189.1 nm) and the porosity was 67.6 %.

[0202] The pellets were tested by exposing them to 50 cycles of the CO₂ sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO₂ sorption capacity of 38 mass %. The CO₂ sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.1 lbf/mm (4.9 N/mm) to 3.1 lbf/mm (13.8 N/mm) after 50 cycles.

[0203] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO₂ sorption capacity. These pellets can be made by the present method.

Example 6

[0204] In example 6, CaO-calcium aluminate pellets were prepared according to the present method. A mixture was prepared by mixing 100g of calcium carbonate, 15.2g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaCO_3 and alumina in the mixture was sufficient to (a) stoichiometrically produce a nominal composition of $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and (b) provide sufficient amount of CaO to produce CaO-calcium aluminate containing 69 wt% free CaO. The particle size of calcium carbonate and alumina powders was about 10 microns. Approximately 49g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled down to room temperature to form the pellets in final form.

[0205] XRD analysis of the fresh pellets identified CaO as the major phase with $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 as minor phases.

[0206] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 36427 angstroms (3642.7 nm) and the porosity was 72 %.

[0207] The pellets were tested by exposing them to 50 cycles of the CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 36 mass %. The CO_2 sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.5 lbf/mm (6.7 N/mm) to 3.3 lbf/mm (14.7 N/mm) after 50 cycles.

[0208] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO_2 sorption capacity. These pellets can be made by the present method.

Example 7

[0209] In example 7, CaO-calcium aluminate pellets were prepared according to the present method. A mixture was prepared by mixing 100g of calcium carbonate, 22.9g of alumina in the form of boehmite (75% pure alumina), and 2g methocel as a pore former. The amount of CaCO_3 and alumina in the mixture was sufficient to (a) stoichiometrically produce a nominal composition of $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and (b) provide sufficient amount of CaO to produce CaO-calcium aluminate containing 57 wt% free CaO. The particle size of calcium carbonate and alumina powders was about 10 microns. Approximately 49g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled down to room temperature to form the pellets in final form.

mina), and 2g methocel as a pore former. The amount of CaCO_3 and alumina in the mixture was sufficient to (a) stoichiometrically produce a nominal composition of $3\text{CaO} \cdot 2\text{Al}_2\text{O}_3$ and (b) provide sufficient amount of CaO to produce CaO-calcium aluminate containing 57 wt% free CaO. The particle size of calcium carbonate and alumina powders was about 10 microns. Approximately 49g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium aluminate in-situ. The calcined pellets were then cooled down to room temperature to form the pellets in final form.

[0210] XRD analysis of the fresh pellets identified CaO as the major phase with $\text{Ca}_3\text{Al}_2\text{O}_6$ and CaAl_2O_4 as minor phases.

[0211] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 19868 angstroms (1986.8 nm) and the porosity was 66.7 %.

[0212] The pellets were tested by exposing them to 50 cycles of the CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 30 mass %. The CO_2 sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.5 lbf/mm (6.7 N/mm) to 3.3 lbf/mm (14.7 N/mm) after 50 cycles.

[0213] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO_2 sorption capacity. These pellets can be made by the present method.

Example 8

[0214] In example 8, CaO-calcium titanate pellets were prepared according to the present invention. A mixture was prepared by mixing 90g of calcium carbonate, 23.6g of CaO (prepared by decomposing calcium carbonate at 900°C), and 60g of titanium dioxide. The amount of CaO and titanium dioxide in the mixture was sufficient to stoichiometrically produce CaTiO_3 . In addition, the amount of calcium carbonate, CaO, and alumina in the mixture was sufficient to produce CaO-calcium titanate containing 38 wt% free CaO. The particle size of

calcium carbonate, CaO and titanium dioxide powders was about 10 microns. Close to 48g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pellets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium titanate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in final form.

[0215] XRD analysis of the fresh sample identified a phase mixture of CaTiO_3 , CaO, and minor amount of TiO_2 .

[0216] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 15235 angstroms (1523.5 nm) and the porosity was 69.8 %.

[0217] The pellets were tested by exposing them to 50 cycles of the CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 32 wt %. The CO_2 sorption capacity of the pellets did not change even after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.2 lbf/mm (5.3 N/mm) to 1.8 lbf/mm (8.0 N/mm) after 50 cycles.

[0218] This example demonstrates that the pellets described herein are strong and dimensionally stable and retain their CO_2 sorption capacity. These pellets can be made by the present method.

Example 9

[0219] In example 9, CaO-calcium titanate pellets were prepared according to the present invention. A mixture was prepared by mixing 90g of calcium carbonate, 12.4g of CaO (prepared by decomposing calcium carbonate at 900°C), 16.3g of titanium dioxide, and 2g of methocel as a pore former. The amount of CaO and titanium dioxide in the mixture was sufficient to stoichiometrically produce CaTiO_3 . In addition, the amount of calcium carbonate, CaO, and alumina in the mixture was sufficient to produce CaO-calcium titanate containing 64 wt% free CaO. The particle size of calcium carbonate, CaO and titanium dioxide powders was about 10 microns. Approximately 36g of deionized water was added to the mixture to prepare a paste. The paste was then used to prepare 1/16 inch (0.16 cm) diameter green pel-

lets by extruding in a lab-scale extruder. The green pellets were dried at 120°C. They were heated at 2°C/minute from room temperature to 600°C in a furnace in air. The calcination temperature was maintained at 600°C for 30 minutes to consolidate the structure of the green pellets. The pellets were then heated at 0.5°C/minute from 600°C to 700°C. The green pellets were maintained at 700°C for 30 minutes to further consolidate the structure of the pellets. The green pellets were then heated at a heating rate of 0.5°C/minute from 700°C to 1000°C. The pellets were maintained at 1000°C for 2 hours to form calcium titanate in-situ. The calcined pellets were then cooled to room temperature to form the pellets in final form.

[0220] The median pore diameter and porosity was measured by mercury porosimetry. The median pore diameter for a representative sample was 13646 angstroms (1364.6 nm) and the porosity was 69.8 %.

[0221] The pellets were tested by exposing them to 50 cycles of CO_2 sorption/desorption in the TGA using a humidified atmosphere described above. Both the sorption and desorption were carried out at 750°C. These pellets showed an initial CO_2 sorption capacity of 38 mass % with a CO_2 sorption capacity of 21 mass % after 50 cycles. The diameter of pellets did not change after 50 sorption and desorption cycles. Furthermore, the crush strength of the pellets increased from 1.6 lb/mm (7.1 N/mm) to 2.2 lb/mm (9.8 N/mm) after 50 cycles.

[0222] This example demonstrates that the pellets described herein are strong and dimensionally stable. These pellets can be made by the present method.

[0223] This example illustrates that strong and dimensionally stable CaO-calcium titanate pellets can be prepared by the method described above. While the CO_2 sorption capacity decreased after 50 cycles of CO_2 sorption/desorption, the final CO_2 sorption capacity is still much greater than that of Example 1 and Example 2, which were pellets not made by the present method.

[0224] The above described specific embodiments and examples are merely illustrative of the invention, which is not limited thereto.

Claims

1. An aggregate suitable for carbon dioxide sorption comprising:

25 to 85 mass % of at least one binding agent selected from calcium titanate, calcium aluminate, calcium zirconate, magnesium titanate, magnesium aluminate, and magnesium zirconate; and

15 to 75 mass % of calcium oxide, magnesium oxide or mixture of calcium oxide and magnesium oxide;

wherein the aggregate is a pellet or a granule having a median pore diameter in a range of 500 nm to 5000 nm and a porosity in a range of 45

% to 80 %.

2. The aggregate of claim 1 further comprising:
0.1 to 10 mass % of at least one metal selected from
Ni, Pt, Rh, and Pd. 5
3. The aggregate of claim 1 or claim 2 wherein the ag-
gregate is a pellet and has a characteristic length of
0.1 mm to 3 mm. 10
4. The aggregate of any one of claims 1 to 3 wherein
the aggregate is a pellet and has a crush strength of
4 to 67 N/mm (1 to 15 lbf/mm) as determined in ac-
cordance with ASTM standard test method D
6175-03. 15
5. The aggregate of any one of claims 1 to 4 wherein
the aggregate is a pellet and has a structure wherein
the crush strength of the pellet is retained within 4
to 67 N/mm (1 to 15 lbf/mm) after 50 cycles of CO₂
sorption and CO₂ desorption wherein the CO₂ sorp-
tion is by exposing the pellet to a humidified
CO₂-containing gas comprising 97 to 98 vol. % CO₂
and 2 to 3 vol. % H₂O at 750°C and CO₂ desorption
is by exposing the pellet to humidified air at 750°C. 20 25
6. The aggregate of claim 1 or claim 2 wherein the ag-
gregate is a granule and has a characteristic length
of 50 microns to 3 mm. 30
7. The aggregate of any one of claims 1, 2, or 6 wherein
the aggregate is a granule and has a structure where-
in the granule retains its shape and size after 50 cy-
cles of CO₂ sorption and CO₂ desorption wherein
the CO₂ sorption is by exposing the granule to a hu-
midified CO₂-containing gas comprising 97 to 98 vol.
% CO₂ and 2 to 3 vol. % H₂O at 750°C and CO₂
desorption is by exposing the granule to humidified
air at 750°C. 35 40
8. A method for making an aggregate suitable for car-
bon dioxide sorption, the method comprising the
steps of: 45
 - (a) preparing a mixture, the mixture comprising: 45
 - at least one of calcium carbonate and mag-
nesium carbonate in an amount to provide
the 15 to 75 mass % of calcium oxide, mag-
nesium oxide or mixture of calcium oxide
and magnesium oxide in the aggregate; 50
 - at least one of a calcium precursor and a
magnesium precursor in an amount to pro-
vide the 25 to 85 mass % of the at least one
binding agent in the aggregate; 55
 - at least one of TiO₂, Al₂O₃, ZrO₂, Al(OH)₃
and AlO(OH) in an amount to provide the
25 to 85 mass % of the at least one binding

agent in the aggregate; and
20 to 80 mass % water;

- (b) forming a green aggregate from the mixture;
- (c) heating the green aggregate from a first tem-
perature to a second temperature at a first av-
erage heating rate of 0.1°C/minute to 10°C/
minute,
wherein the first temperature is within a first tem-
perature range wherein the first temperature
range is between 5°C and 50°C, and
wherein the second temperature is a minimum
temperature of a second temperature range, the
second temperature range extending from the
minimum temperature of the second tempera-
ture range to a maximum temperature of the sec-
ond temperature range wherein the minimum
temperature of the second temperature range
is 600°C and the maximum temperature of the
second temperature range is 750°C;
- (d) maintaining the green aggregate within the
second temperature range for a first time period
of between 15 minutes and 4 hours;
- (e) heating the green aggregate from the maxi-
mum temperature of the second temperature
range to a third temperature at a second average
rate of 0.1°C/minute to 10°C/minute,
wherein the third temperature is a minimum tem-
perature of a third temperature range, the third
temperature range extending from the minimum
temperature of the third temperature range to a
maximum temperature of the third temperature
range wherein the minimum temperature of the
third temperature range is 900°C and the max-
imum temperature of the third temperature
range is 1050°C;
- (f) maintaining the green aggregate within the
third temperature range for a second time period
of between 15 minutes and 4 hours; and
- (g) cooling the green aggregate to a fourth tem-
perature, wherein the fourth temperature is with-
in a fourth temperature range wherein the fourth
temperature range is between 0°C and 50°C, to
make the aggregate;
wherein the green aggregate is exposed to an
atmosphere comprising oxygen during at least
one of steps (a) through (f).
9. The method of claim 8 wherein the mixture compris-
es 20 to 40 mass % water and
wherein the green aggregate is a green pellet and
the aggregate is a pellet.
10. The method of claim 8 or claim 9 wherein the green
aggregate is exposed to the atmosphere comprising
oxygen during all of steps (a) through (f).
11. The method of any one of claims 8 to 10 wherein the

mixture further comprises 0.1 to 10 mass % of at least one metal selected from Ni, Pt, Rh, and Pd.

12. The aggregate of any one of claims 1 to 7 made by the method of any one of claims 8 to 11.

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13. An apparatus for producing a CO₂-depleted gas from a CO₂-containing gas, the apparatus comprising:

a bed containing a plurality of CO₂-sorptive aggregates, wherein the plurality of CO₂-sorptive aggregates comprise an aggregate as claimed in any one of Claims 1 to 7 or Claim 12.

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14. A process for producing a CO₂-depleted gas from a CO₂-containing gas in an apparatus as claimed in Claim 13, the process comprising:

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(i) passing the CO₂-containing gas through the bed under conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate with the plurality of aggregates and thereby forming the CO₂-depleted gas;

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(ii) regenerating the bed by passing a purge gas through the bed under conditions sufficient to liberate CO₂ from the plurality of aggregates and withdrawing a by-product gas comprising CO₂ from the apparatus; and

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(iii) repeating (i) and (ii) in a cyclic manner.

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15. The process of claim 14 wherein the conditions sufficient to sorb CO₂ and form calcium carbonate and/or magnesium carbonate include a temperature ranging from 600°C to 800°C and a pressure ranging from 1 to 100 bar (1 to 100 atmospheres), and wherein the conditions sufficient to liberate CO₂ include a temperature ranging 650°C to 900°C and a pressure ranging from 0.9 to 100 bar (0.9 to 100 atmospheres), and wherein the purge gas comprises at least one of nitrogen and steam and the purge gas optionally comprises oxygen.

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16. A reactor for producing a hydrogen-containing gas, the reactor comprising:

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a bed containing CO₂-sorptive aggregates, optionally containing steam-hydrocarbon reforming catalyst aggregates comprising a reforming catalyst, and optionally containing a metal oxide of at least one of Cu, Fe and Ni, wherein the CO₂-sorptive aggregates are the aggregates as claimed in any one of Claims 1 to 7 or Claim 12, and wherein if the bed does not contain the steam-hydrocarbon reforming catalyst aggregates and does not contain the metal oxides, then at least a plurality of the CO₂-sorptive aggregates include the at least one metal selected

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from Ni, Pt, Rh and Pd.

17. A process for producing a hydrogen-containing gas in a reactor as claimed in Claim 16, the process comprising:

(i) in a production step, introducing steam and a feed gas containing methane into the reactor, reacting the methane and the steam in the bed in the presence of at least one of the reforming catalyst, the metal oxide and the at least one metal under reaction conditions sufficient to form hydrogen, sorb CO₂ and form calcium carbonate and/or magnesium carbonate, and withdrawing a product gas comprising hydrogen from the reactor;

(ii) in a regeneration step, regenerating the CO₂-sorptive aggregates by passing a purge gas through the bed under conditions sufficient to liberate CO₂ from the CO₂-sorptive aggregates and withdrawing a by-product gas comprising CO₂ from the reactor; and

(iii) repeating (i) and (ii) in a cyclic manner.

18. The process of claim 17 wherein the reaction conditions sufficient to form hydrogen, sorb CO₂ and form calcium carbonate and/or magnesium carbonate include a temperature ranging from 350°C to 800°C and a pressure ranging from 1 to 100 bar (1 to 100 atmospheres), and wherein the conditions sufficient to liberate CO₂ include a temperature ranging 450°C to 900°C and a pressure ranging from 0.9 to 100 bar (0.9 to 100 atmospheres), and wherein the purge gas comprises at least one of nitrogen and steam and the purge gas optionally comprises oxygen.

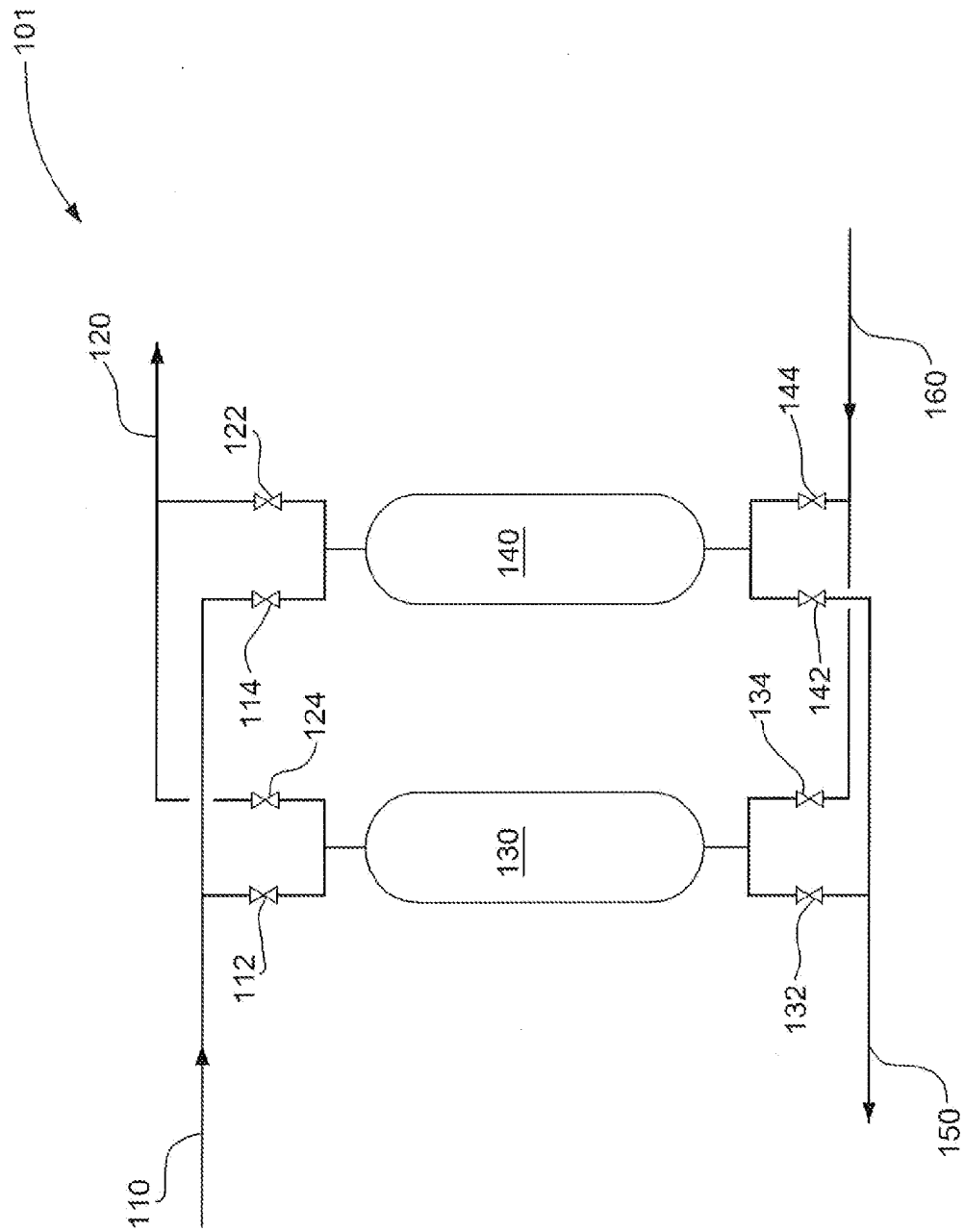


FIG. 1

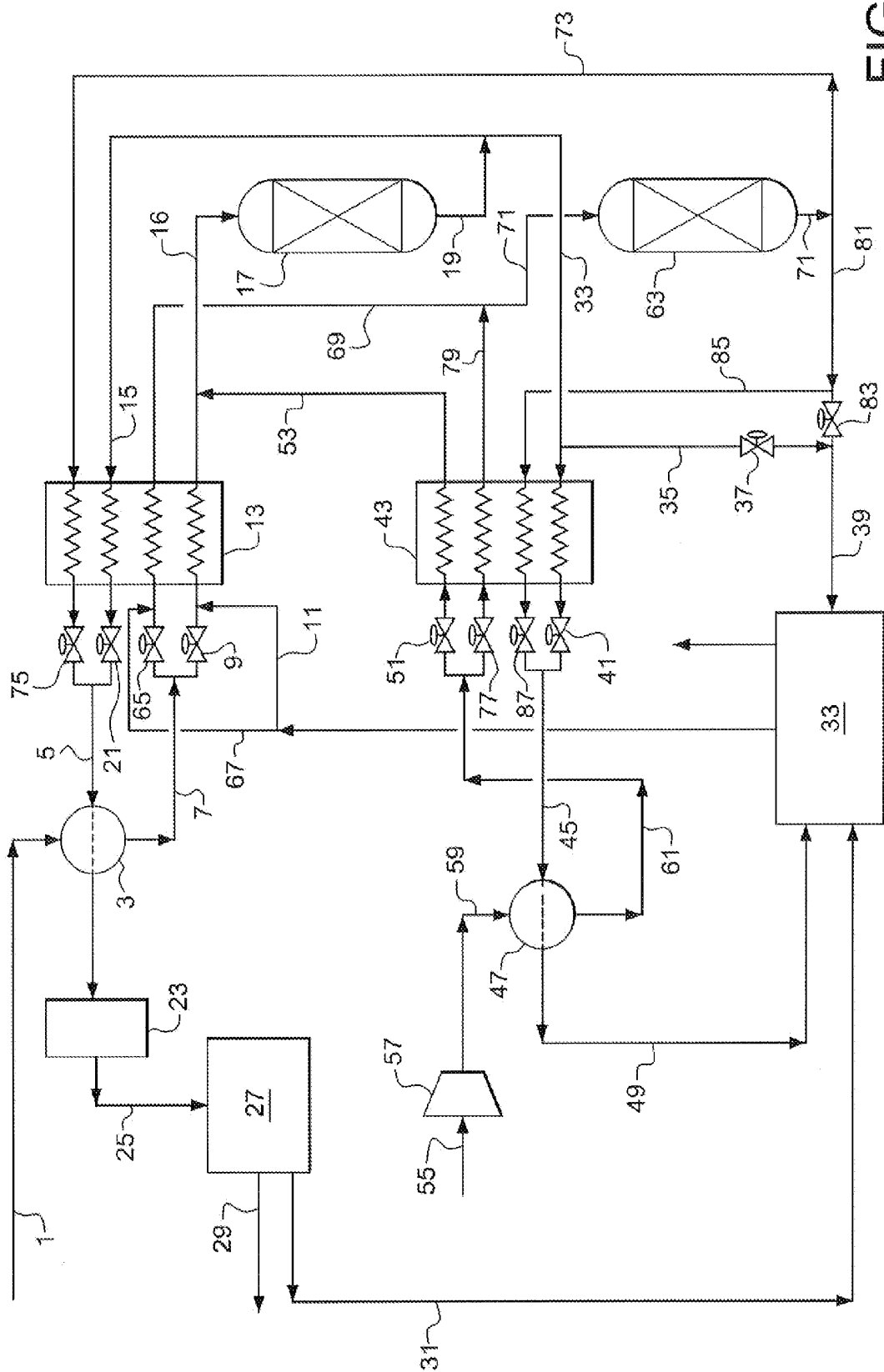


FIG. 2

REFERENCES CITED IN THE DESCRIPTION

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(Continua na página seguinte)

(54) Title : CERAMIC MATERIALS FOR ABSORBING ACID GASES, PROCESS OF PREPARING SAME AND CYCLIC ACID GAS ABSORPTION AND REGENERATION PROCESS

(54) Título : MATERIAIS CERÂMICOS PARA ABSORÇÃO DE GASES ÁCIDOS, PROCESSO DE PREPARAÇÃO DOS MESMOS E PROCESSO CÍCLICO PARA A ABSORÇÃO E REGENERAÇÃO DE GASES ÁCIDOS

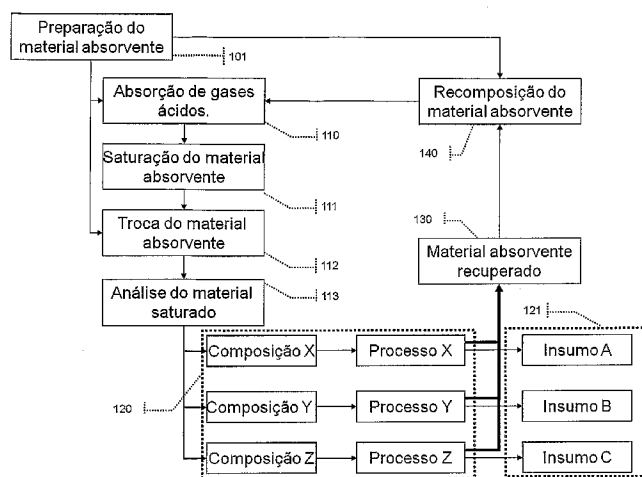


Figura 1

- 101 Preparation of absorbent material
- 110 Absorption of acid gases
- 111 Saturation of absorbent material
- 112 Replacement of absorbent material
- 113 Analysis of saturated material
- 120 X composition; X process
Y composition; Y process
Z composition; Z process
- 121 A raw material
B raw material
C raw material
- 130 Retrieved absorbent material
- 140 Recomposition of absorbent material

(57) Abstract : The present invention describes a process for preparing ceramics for the absorption of acid, greenhouse effect gases released in combustion systems, or present in closed environments. In relation to carbon dioxide, the principal target of the present invention, the process of absorption, transport, processing and transformation of the gas into other products is described. The process uses ceramic materials prepared by mixing one or more solid metallic oxides with one or more binding agents and an expanding agent. The resulting product can be processed and the absorbent system regenerated. The carbon dioxide obtained in the process can be used as analytic or commercial carbonic gas, various carbamates and ammonium carbonate.

(57) Resumo :

(Continua na página seguinte)

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A presente invenção descreve o processo de preparação de cerâmicas para absorção de gases ácidos, agravantes do efeito estufa, que são liberados em sistemas de combustão, ou que estão presentes em ambientes fechados. Em relação ao dióxido de carbono, alvo principal da presente invenção, é descrito um processo de absorção, transporte, processamento e transformação do gás em outros produtos. O processo utiliza materiais cerâmicos preparados através da mistura sólida de um ou mais óxidos metálicos, com um ou mais agentes aglomerantes e um agente expansivo. O produto gerado pode ser processado e o sistema absorvente regenerado. O dióxido de carbono obtido no processamento pode ser empregado como gás carbônico analítico ou comercial, carbamatos diversos e carbonato de amônio.

**“MATERIAIS CERÂMICOS PARA ABSORÇÃO DE GASES ÁCIDOS,
PROCESSO DE PREPARAÇÃO DOS MESMOS E PROCESSO CÍCLICO
PARA A ABSORÇÃO E REGENERAÇÃO DE GASES ÁCIDOS”**

CAMPO DE APLICAÇÃO

5 A presente invenção descreve o processo de preparação de cerâmicas para absorção de gases ácidos, agravantes do efeito estufa, que são liberados em sistemas de combustão, ou que estão presentes em ambientes fechados. Em relação ao dióxido de carbono, alvo principal da presente invenção, é descrito um processo de absorção, transporte, processamento e transformação
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15 carbamatos diversos e carbonato de amônio.

ESTADO DA TÉCNICA

 A emissão de gases de efeito estufa tais como metano (CH_4), dióxido de carbono (CO_2), dióxido de enxofre (SO_2), trióxido de enxofre (SO_3) e óxidos nitrogenados, bem como compostos hidrocarbonetos (HC) tem provocado uma
20 série de mudanças climáticas que são desfavoráveis à manutenção da vida. Podem-se citar fenômenos tais como o prolongamento de períodos de estiagem, formação de tempestades de dimensões catastróficas, furacões e tornados em regiões que não apresentavam esses tipos de fenômenos climáticos, além da elevação global da temperatura da atmosfera e dos oceanos. Associados a
25 essas modificações climáticas existem também a formação de chuva ácida que é intensificada pela presença de gases ácidos e a poluição intrínseca encontrada na forma de material particulado e substâncias tóxicas, que passam a fazer parte da atmosfera que está em contato direto com praticamente todos os organismos aeróbicos presentes na biosfera.

30 As emissões de gases de efeito estufa são provocadas principalmente pelos métodos industriais presentes em setores estratégicos da economia global, tais como a indústria siderúrgica, indústria de cimentos, termoeletricas, dentre outras. Para os grandes centros urbanos destaca-se outro agravante, que

compreende a emissão de gases poluentes provenientes dos meios de transporte que utilizam combustíveis baseados no carbono (gasolina, diesel, gás natural, álcool), sendo que os combustíveis de origem fóssil (gasolina, diesel, carvão mineral) são consideravelmente mais poluentes que os combustíveis
5 provenientes de fontes renováveis (álcool e biodiesel).

Projeções climáticas futuras sinalizam a necessidade imediata da implementação de procedimentos eficazes para o controle de emissões de gases poluentes. A utilização de tecnologias ambientalmente corretas tendo como base a energia solar, hidrogênio, energia eólica, etc. está ainda longe do
10 alcance dos processos industriais. A utilização de fontes energéticas renováveis e baseadas no carbono, como por exemplo, etanol ou biodiesel, aumentam a eficiência energética, diminuindo as emissões de gases de efeito estufa, principalmente de dióxido de carbono (CO₂), mas sempre emitirão uma quantidade intrínseca de CO₂ durante o processo de queima, que é inerente à
15 reação química de combustão. O desenvolvimento desse tipo de tecnologia, destinada à redução das emissões de gases de efeito estufa, tem sido incentivado por políticas públicas que atribuem metas para as emissões de gases, como exemplo a união européia, que estabeleceu um limite de 120 g/km de CO₂ para veículos de passageiros até o ano de 2012, sendo que a taxa atual
20 corresponde a 160 g/km. Assim, o cumprimento dessa meta irá representar uma redução de 25% da poluição provocada por veículos leves, que contribuem atualmente com aproximadamente 15% de toda a poluição mundial. Outras legislações específicas estabelecem taxas máximas de emissões para plantas industriais tais como indústria siderúrgica e indústria de cimento, além da
25 tributação referente ao processo como método poluente. Entretanto, todas essas restrições legais impostas aos sistemas produtivos que emitem gases de efeito estufa, não são suficientes para impedir o crescimento dos níveis de gases poluentes emitidos, como pode ser verificado pelos relatórios da ONU (<http://www.onu-brasil.org.br>, 12/2008). Vale acrescentar que a maior
30 contribuição para a poluição mundial vem das indústrias, que correspondem a aproximadamente 70% (<http://gaoli.sites.uol.com.br/arpolu.htm>, 12/2008) da poluição mundial.

Relacionado ainda com o desenvolvimento de políticas de incentivos à redução das taxas de emissão de gases de efeito estufa, pode-se citar o

protocolo de KYOTO, que sugere aos países mais desenvolvidos, que são os responsáveis por mais da metade das emissões no mundo, a fomentar e implementar tecnologias que reduzam a quantidade de gases de efeito estufa em seu próprio território ou em outros países. O financiamento destas

5 tecnologias é recompensado através dos créditos de carbonos, sendo estabelecido que uma tonelada de CO₂ não emitida, ou retirada da atmosfera, corresponde a um crédito de carbono, avaliado atualmente (2009) em R\$30,00 reais (<http://www.pointcarbon.com/>, 27/10/2009). Assim, empresas que desenvolvem metodologias ambientalmente adequadas ao protocolo de KYOTO

10 ou, que tenham em seus objetivos a descontaminação da atmosfera poderão captar recursos através da venda em mercados acionários de créditos de carbono.

O objetivo de diversas tecnologias dedicadas à redução das emissões de gases poluentes consiste em impedir que estes sejam liberados para a

15 atmosfera através de tratamentos químicos que podem imobilizá-los em uma fase condensada (líquida ou sólida).

Sendo o dióxido de carbono o principal poluente e maior agravante do efeito estufa, existem diversas tecnologias descritas no estado da técnica que propõem métodos para a redução da sua quantidade emitida. De forma geral,

20 essas metodologias estão focadas em dois objetivos, sendo o primeiro relacionado ao aprisionamento permanente do CO₂ e o segundo relacionado à reutilização do CO₂ para a produção de insumos e/ou produtos de interesse industrial.

Para demonstrar a relevância do processo e a complexidade da absorção

25 de gases ácidos produzidos em sistemas de combustão ou presentes em ambientes fechados, diversas patentes, metodologias e aparatos podem ser encontrados no estado da técnica. Inicialmente as invenções tinham por objetivo absorver gases tóxicos em ambientes fechados, como por exemplo, submarinos e aparelhos de respiração com refluxo de gases anestésicos. Para a purificação

30 do ar em submarinos (absorção de CO₂) o documento GB 190603570 (Winand, P.; "Process for the Elimination of Carbon Dioxide from the Gaseous Combustion Products of Combustion Engines", 1906) descreve uma mistura absorvente de amônia com óxido de sódio ou óxido de potássio, sendo que esses são produzidos durante a geração do comburente O₂, em motores de combustão

interna que são destinados à propulsão de submarinos. Relacionado ainda à atmosfera de submarinos, a patente US 2,545,194 (Colburn, A. P.; Dodge, B.; "Adsorption process for removal of carbon dioxide from the atmosphere of a submarine", 1951) descreve a utilização apenas de óxido de lítio (Li_2O) para absorção de CO_2 , pois uma quantidade menor de massa é suficiente para a manutenção da qualidade do ar para a tripulação. Com o desenvolvimento de tecnologias para a exploração espacial, a absorção de CO_2 em ambientes fechados assume uma posição de elevada relevância, como é demonstrado pela patente US 7,326,280 (Hrycak, M. B.; McKenna, D. B.; "Enhanced carbon dioxide adsorbent", 2005) aplicada em sistemas de purificação de naves (foguetes) e estações espaciais com a utilização do óxido de lítio.

A aplicação em larga escala de processos de absorção de dióxido de carbono em ambientes fechados pode ser demonstrada pela patente US 5,087,597 (Orlando, L. e colaboradores; Carbon dioxide adsorbent and method for producing the adsorbent, 1992) com a descrição de uma mistura à base de polialcoxissilano, sílica, alumina e óxido de ferro, que é empregada na absorção de CO_2 presente em contêineres para transporte de materiais susceptíveis à decomposição por ambiente ácido ou para o transporte de animais.

Outra aplicação de grande importância corresponde à absorção de CO_2 em aparelhos de anestesia gasosa. Estes aparelhos devem apresentar um sistema para a absorção do CO_2 expirado pelo paciente; entretanto, os materiais absorventes não podem reagir com as substâncias anestésicas, como ocorre em sistemas de absorção de compostos por óxidos de metais alcalinos. Neste caso, o documento BR 9713138 (Amstrong, J. R.; Murray, J.; "Absorvente de dióxido de carbono para uso em anestesiologia, e, processo de preparação do mesmo", 1997) propõe a substituição da cal soldada por uma mistura de hidróxido de cálcio, gesso e alumínio e um agente higroscópico (cloreto de cálcio). Semelhantemente, o documento RU 2152251 (Imanenkov, S. I.; Aleksandrova, T. I.; Kulakov, N. I.; Putin, B. V.; "Method of synthesis of carbon dioxide adsorbent", 2000) descreve a utilização de uma mistura de hidróxido de cálcio e carbonato de potássio para absorção de CO_2 em aparelhos respiratórios.

Para aplicações industriais os processos de absorção podem ser realizados de formas mais diversificadas, como, por exemplo, está descrito no

documento BR 0306705 (Johannes, B. T. e colaboradores; "Process for removing carbon dioxide from gas mixtures", 2004) que mostra o emprego de uma mistura composta por água, sulfolano e uma amina secundária ou terciária derivada da etanolamina. O processo de absorção é realizado através da pulverização da
5 solução absorvente contra o fluxo de gás contendo CO_2 , H_2S e/ou COS . O processo descrito deve ser realizado preferencialmente a uma temperatura entre 50°C e 90°C . Para a absorção de CO_2 em fluxos de gases, à temperatura ambiente ou aproximadamente até 100°C , diversas patentes podem ser encontradas descrevendo a utilização de zeólitas em aparatos específicos,
10 como, por exemplo, a patente US 5,531,808 (Ojo A. F.; Fitch, F.R; Buelow, M.; "Removal of carbon dioxide from gas streams", 1996) que utiliza zeólita-X e o documento EP 0173501 (Keith, P. G.; "Process for removing carbon dioxide from gas mixtures", 1986) que utiliza zeólita-A. Os processos de absorção de CO_2 através de Zeólitas são limitados pela faixa de temperatura, devido à fraca
15 interação que a zeólita apresenta com o CO_2 absorvido. Para temperaturas mais elevadas, em que a absorção de CO_2 será efetuada, deve-se utilizar material que não sofra decomposição térmica e que, preferencialmente, seja ativado pelo aumento da temperatura, como por exemplo é descrito no documento BR 0003340 para a preparação de uma mistura composta por óxido de magnésio e
20 um carbonato de metal alcalino (Mayorga, S. G. e colaboradores; "Adsorventes de dióxido de carbono contendo óxido de magnésio adequado para uso sob altas temperaturas e processo de sua fabricação", 2000). Essa mistura absorve CO_2 em uma faixa de temperatura entre 300°C e 550°C .

Além dos métodos de absorção, existe também o documento US
25 2008086938 (Hazlebeck, D. A.; Dunlop, E. H.; "Photosynthetic carbon dioxide sequestration and pollution abatement"; 2008) que descreve a utilização do CO_2 produzido em plantas industriais para ser injetado em biodigestores contendo algas, que através do processo de fotossíntese realizam a biossíntese de óleos combustíveis de interesse industrial.

30 Alguns métodos paliativos para impedir a liberação de dióxido de carbono na atmosfera também podem ser encontrados, como, por exemplo o documento AU 2008100189 (Ferguson, J. I, S.; "Sequestration of carbon in sinking water" 2008), que sugere um método para a realização de depósitos de CO_2 em profundezas oceânicas, entre 3.000 a 4.000 metros, aproximadamente.

PROBLEMA DO ESTADO DA TÉCNICA

As tecnologias existentes no estado da técnica para a redução de gases ácidos possuem como princípio a imobilização e transporte dos gases para outro local, de modo que o material absorvente saturado deva ser descartado.

5 SOLUÇÃO PROPOSTA

O sucesso das metas e tratados ambientais recentemente propostos será alcançado através do desenvolvimento de tecnologias ambientais eficientes, que possibilitem a reutilização do CO₂ e outros gases poluentes, sem onerar demasiadamente os sistemas produtivos. É justamente com base nessa visão

10 que o presente pedido de patente se fundamenta. É proposto, através da utilização de cerâmicas absorventes para gases ácidos, efetuar um ciclo completo entre a absorção e armazenamento de gases ácidos e finalmente transformá-los em insumos para diversos setores produtivos, como por exemplo, indústria agropecuária e indústria química. Esse ciclo de absorção faz com que

15 a massa de poluentes emitidos seja transferida para uma aplicação industrial, com a recuperação simultânea de parte do material absorvente. Quando esse ciclo não é executado, o material poluente é apenas imobilizado e transportado para outra localidade, ou seja, a poluição é "transferida" para outro lugar, a partir da criação de depósitos de descarte de material absorvente saturado; porém,

20 sem nenhum impacto grave ambiental porque o material formado é inerte ao meio ambiente. Portanto, as metodologias até então disponíveis são ineficazes, já que apenas deslocam o material poluente, por exemplo, gases ácidos. A presente invenção vem justamente cobrir essa lacuna, propondo um ciclo completo que permite armazenar, transportar e regenerar os gases ácidos

25 absorvidos para uso e aplicações diversas. É importante ainda ressaltar o baixo custo da metodologia proposta e ambientalmente correta, sendo inerte ao meio ambiente.

DESCRIÇÃO DETALHADA DA INVENÇÃO

A presente invenção descreve um método de redução das emissões de

30 gases ácidos e agravantes do efeito estufa, que são liberados por sistemas de combustão e plantas industriais tais como indústrias siderúrgicas, indústrias cimenteiras e termoelétricas, ou sistemas de purificação de gases. O material

absorvente, após a sua saturação por gases ácidos, é então processado termicamente ou quimicamente gerando um fluxo de gás purificado, que em seguida é utilizado em processos de síntese de diversos insumos, tais como gás comprimido analítico ou comercial, insumos para indústria química por meio da síntese de carbamatos, ácidos correlatos e insumos para indústria agropecuária com a fabricação de carbonatos, nitratos, sulfatos e sulfitos. O processamento térmico ou químico tem a capacidade de regenerar o material absorvente, gerando assim um ciclo de despoluição atmosférica com a formação de insumos relevantes a diversos setores industriais a um baixo custo.

A presente invenção propõe um conjunto de misturas absorventes contendo óxidos de metais alcalinos terrosos, metais alcalinos ou metais de transição que apresentam uma cinética de reação favorável à absorção de dióxido de carbono e outros gases ácidos, tais como SO_2 , SO_3 , NO e NO_2 , mas não limitantes. As misturas absorventes propostas também contêm o agente aglomerante (endurecedor) e o agente expensor. As diferentes composições apresentadas têm a propriedade de absorver gases ácidos em diferentes temperaturas que podem variar de 25°C a 700°C como será apresentado mais adiante.

Algumas formulações de misturas absorventes descritas no presente pedido de patente têm a capacidade de absorver gases ácidos em diferentes ambientes e condições termodinâmicas variadas, sendo assim eficaz em diversas situações, tanto quando houver necessidade de uma rápida absorção, no caso de absorções moderadas e naquelas em que se necessita uma absorção extremamente lenta. Portanto, a metodologia proposta na presente invenção apresenta um controle tanto termodinâmico quanto cinético. Sendo assim, a tecnologia proposta pode ser aplicada para descontaminação de ambientes fechados à temperatura ambiente ($\sim 25^\circ\text{C}$), purificação de fluxos de gases, absorção de gases de rejeito industrial (sistemas de exaustão) em temperaturas entre 50°C e 600°C , tais como produção de coque, sinterização de materiais, laminação, absorção de gases ácidos liberados pela queima de combustíveis, em motores de combustão interna, além de purificação fluxos de gases de admissão para motores de combustão interna, produção de energia através de termoeletricas, com o objetivo de aumentar a eficiência do processo de queima de combustíveis.

O ciclo de operação dos materiais absorventes está ilustrado na figura 1, sendo possível observar que o acoplamento ideal entre o processo de absorção de gases poluentes de natureza ácida com métodos de reutilização do material absorvente tem a capacidade de reduzir e, até mesmo, extinguir a emissão de gases ácidos em sistemas de combustão, tais como, fornos de queima de combustíveis e motores a combustão interna e plantas industriais. A metodologia propõe um ciclo de reutilização do material absorvente, que, após a sua saturação é recolhido, trocado e analisado para a determinação da composição dos gases absorvidos. Em seguida, a partir da sua composição, o material saturado é conduzido a uma planta industrial implementada para a recuperação do gás absorvido, transformando-o em um insumo industrial, regenerando totalmente ou parcialmente o material absorvente.

A presente invenção descreve a utilização de uma mistura sólida composta por um ou mais óxidos de metais alcalinos terrosos, um ou mais hidróxidos de metais alcalinos e óxidos de metais de transição, acrescidos de agente aglomerante e agente expensor. A mistura destes componentes deve ser feita em meio aquoso para que o sólido final adquira consistência e seja expandido uniformemente através da atuação do agente aglomerante e do agente expensor. Após a completa homogeneização dos componentes, a mistura é mantida em repouso por um período de 1 a 5 horas, para que o agente expensor, tal como alumínio metálico pulverizado ou oxalato de cálcio, possa atuar gerando bolhas uniformes em toda a extensão da massa. A reação do agente expensor é ligeiramente anterior ao agente aglomerante, permitindo assim a formação de bolhas que serão estruturalmente mantidas através da ativação gradual e posterior do agente endurecedor/aglomerante, tal como: óxido de magnésio, bentonita, caulim ou gesso de paris. Após um enrijecimento parcial da mistura, esta é submetida a um processo de aquecimento moderado (100°C - 200°C) por um período entre 3 e 72 horas, não limitante, para a eliminação do excesso de água, passado em seguida para um aquecimento rigoroso (entre 500°C e 800 °C, não limitante) por um período de 1 hora, não limitante, que garante o enrijecimento da mistura. Este aquecimento deve ocorrer na presença de nitrogênio ou na ausência de fluxo de ar, ou seja, em uma câmara fechada ou com a ausência de gases ácidos, que poderiam ser absorvidos durante a síntese do material.

Na etapa posterior à homogeneização, o material pode ser moldado em formatos específicos, como exemplos não limitantes, bloco compacto, bloco vazado (tijolo) ou material pelletizado de gramaturas variadas (5 a 20 mm). Para a moldagem dos blocos (compactos ou vazados) a mistura pode apresentar uma consistência mais fluida através da adição de um excesso de água, facilitando a sua homogeneização. Nesse caso, pode-se também utilizar uma quantidade maior de agente expensor, para aumentar a área e a eficiência do processo de absorção. Para a moldagem do material pelletizado, a mistura inicial deve apresentar uma consistência mais pastosa que possibilite a confecção das pelotas, que em seguida deverão ser submetidas ao aquecimento impedindo a reaglutinação do material.

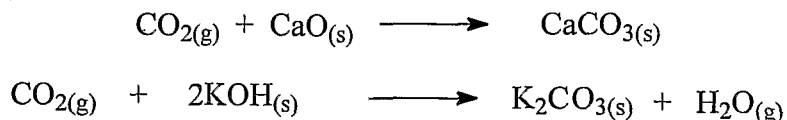
A etapa de aquecimento rigoroso pode ser realizada em autoclave a uma temperatura mais baixa, de aproximadamente 200°C, não limitante. Este processo garante uma maior rigidez do sólido formado, concedendo a este maior resistência mecânica.

O material absorvente descrito neste pedido de patente apresenta um caráter básico, permitindo a sua utilização em processos de absorção de gases ácidos, tais como dióxido de carbono (CO_2), dióxido de enxofre (SO_2), trióxido de enxofre (SO_3), não limitantes. Embora todos os gases citados promovam o agravamento do efeito estufa e das chuvas ácidas, o dióxido de carbono mostra-se como o principal poluente, devido principalmente à elevada quantidade produzida em indústrias que utilizam processos de combustão. Desta forma, o CO_2 será utilizado em exemplificações por meio de reações e exemplos que ilustram a eficiência do processo de absorção para redução das emissões de gases agravantes do efeito estufa, e posterior utilização do material formado, de modo a regenerar a cerâmica absorvente e gerar produtos importantes, de alto valor agregado para diversos setores industriais.

O potencial de absorção dos materiais é determinado pela cinética de reação do gás com os óxidos presentes. Assim, cada mistura apresenta uma faixa de temperatura ideal para absorção, e uma velocidade de absorção que depende da composição, da temperatura e do fluxo de gás sobre o material. As faixas de temperatura de absorção e as condições de regeneração do material serão discutidas posteriormente e individualmente para cada tipo de composição. Como descrito anteriormente, o foco principal desta presente

invenção é a absorção de dióxido de carbono, não limitante; portanto, seguem abaixo as equações que representam as reações químicas que ocorrem durante o processo de absorção do CO₂, a partir de uma mistura absorvente contendo óxido de cálcio e hidróxido de potássio, não limitantes.

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O material absorvente viabiliza o transporte e a concentração de gases absorvidos para instalações industriais apropriadas ao seu processamento. A recuperação do dióxido de carbono pode ser realizada através da decomposição térmica do material, ou a partir do tratamento químico com ácido nítrico, não limitante, e posterior regeneração do material absorvente através da adição de hidróxido de sódio, não limitante, na presença de 1-2% de alumínio, não limitante. A mistura formada é filtrada e aquecida até 100 °C para a eliminação de água, regenerando assim o material absorvente.

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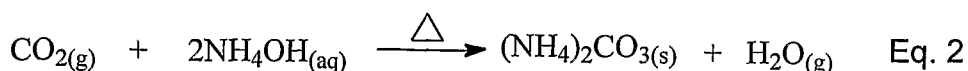
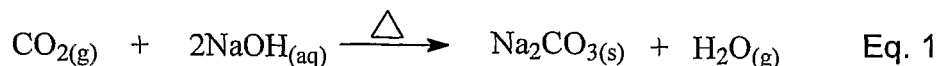
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O dióxido de carbono formado a partir da cerâmica absorvente saturada apresenta uma concentração elevada, viabilizando diversos métodos industriais. Inicialmente o próprio dióxido de carbono pode ser comprimido e engarrafado para a sua posterior comercialização como reagente analítico, ou em processos distintos que empreguem CO₂ gasoso. Além desta aplicação direta do CO₂ que foi absorvido de plantas industriais poluidoras, outros dois métodos, não limitantes, são propostos neste pedido de patente para a transformação química do dióxido de carbono em carbonatos e carbamatos diversos, não limitante.

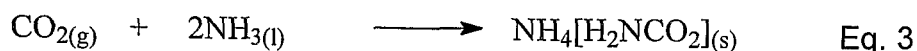
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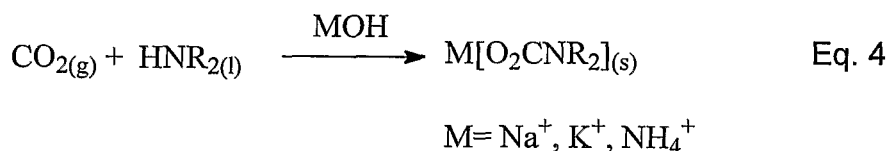
O dióxido de carbono gasoso pode ser injetado em uma solução básica de hidróxido de sódio ou hidróxido de amônio, não limitantes. As reações químicas para estes processos estão apresentadas nas equações 1 e 2 (Eq. 1 e Eq. 2). Após a formação do carbonato, a solução de carbonato de sódio é aquecida até a evaporação completa da água (aproximadamente 100°C), e a de carbonato de amônio (quando a solução básica utilizada é hidróxido de amônio) é deixada evaporar a 40°C para evitar a sublimação do material desejado, restando apenas o carbonato correspondente à base utilizada.



A síntese do carbamato de amônio pode ser realizada à temperatura ambiente através da passagem do fluxo de CO₂ por um recipiente contendo amônia líquida. A reação é cineticamente favorável, sendo perceptível a formação imediata de um sólido branco, correspondente ao carbamato de amônio. Em seguida, o sistema é mantido em repouso e o carbamato pode ser separado por filtração ou decantação, mas não limitante. A reação correspondente a esse processo é apresentada através da equação química a seguir (Eq. 3).



Caso o CO₂ seja coletado em um recipiente contendo uma solução básica aquosa ou em suspensão de aminas secundárias, HNR₂, obtém-se ao final o carbamato de metais alcalinos ou de amônio correspondente, de acordo com a equação a seguir (Eq. 4).



EXEMPLO 1: Preparação do material absorvente Classe 1: Teste da velocidade de absorção e tempo de saturação para 90%

As cerâmicas absorventes da classe 1 utilizam como aglomerante o MgO, com uma concentração de até 10% (p/p) e pó de alumínio como agente expansivo, com uma concentração de até 1%, e o restante da mistura que corresponde aos componentes absorventes é composta por misturas de CaO e La₂O₃ (Fig 3), CaO e KOH (Fig 4), CaO e MgO (Fig 5), MgO e KOH (Fig 6) com as proporções em massa definidas para toda a faixa de temperatura em que o processo de absorção é mais intenso do que o processo de decomposição térmica do material saturado. As misturas contendo magnésio absorvem mais eficazmente entre 50 e 400°C enquanto que as misturas CaO+La₂O₃ e CaO+KOH podem ser empregadas em processo de absorção entre 100 e 700°C. A utilização do MgO como aglomerante concede ao material uma resistência mecânica superior em relação aos aglomerantes bentonita e caulim, como por exemplo, temos que uma esfera de diâmetro aproximado de 5 mm, contendo CaO 75% e MgO 25%, resiste até 55N.

Para as composições da classe 1 o potencial de absorção é maximizado, pois o material aglomerante (MgO) também tem a capacidade de absorver CO₂.

A partir do estudo cinético dos materiais da classe 1 foi possível estimar o tempo de armazenamento (t_{90}) dos materiais absorventes, ou seja o tempo para o consumo de 10% do material armazenado em condições ambientes, para as composições com teor de CaO maior ou igual a 80% é de aproximadamente 15 dias, o que possibilita a estocagem e o transporte do material cerâmico para as instalações industriais onde será aplicada para a absorção de CO₂.

EXEMPLO 2: Preparação do material absorvente Classe 2: Bentonita

As cerâmicas absorventes da classe 2 utilizam como aglomerante a bentonita com uma concentração de até 10% (p/p) e pó de alumínio como agente expansivo com uma concentração de até 1%, e o restante da mistura que corresponde aos componentes absorventes é composta por misturas binárias de CaO e La₂O₃ (Fig 7), o CaO e o KOH (Fig 8), o CaO e o MgO (Fig 9). A bentonita é constituída por 66,9% de SiO₂; 16,3% de Al₂O₃ e 6% de H₂O, sendo as impurezas mais comuns o Fe₂O₃ (~3,3%), o NaOH (2,6%), o Ca(OH)₂ (1,8%) e o Mg(OH)₂ (1,5%). Como mencionado anteriormente a resistência mecânica do material utilizando bentonita (Tabela 1) é inferior em relação ao MgO como aglomerante, mas não incapacita a sua utilização como agente estruturante para misturas absorvente de CO₂. De forma semelhante, as composições contendo CaO+KOH ou CaO+La₂O₃ absorvem em uma faixa de temperatura maior (100 a 700°C), enquanto que a mistura CaO+MgO pode absorver entre 50 e 400°C.

Tabela 1: Teor de bentonita e resistência mecânica para misturas contendo 80% ou mais de CaO

Teor de bentonita (% p/p)	Resistência (N)	Diâmetro da esfera (mm)
10	31	5.8
8	44	6.0
6	41	7.4
4	35	6.9
2	28	6.5

EXEMPLO 3: Preparação do material absorvente Classe 3: Caulim

As cerâmicas absorventes da classe 3 utilizam como aglomerante o caulim com uma concentração de até 10% (p/p) e pó de alumínio como agente expansivo com uma concentração de até 1%, e o restante da mistura que corresponde aos componentes absorventes é composta por misturas binárias de CaO e La_2O_3 (Fig 10), de CaO e KOH (Fig 11), de CaO e MgO (Fig 12). Esta classe de materiais apresenta propriedades físicas e cinéticas semelhantes à classe 2. O caulim corresponde a uma mistura de aluminossilicatos com de fórmula empírica $\text{Al}_2\text{O}_3 \cdot m\text{SiO}_2 \cdot n\text{H}_2\text{O}$, sendo que m pode assumir valores de 1 a 3 e n pode variar entre 2 e 4.

Para exemplificar a eficiência e a velocidade do processo de absorção dos materiais da classe 2, foi utilizada uma composição contendo 88,5% de CaO, 1% de KOH, 10% de caulim e 1% de alumínio. O experimento de absorção foi realizado com um fluxo de CO_2 proporcional à massa do absorvente, compreendendo 26 gramas de CO_2 por minuto por grama de material cerâmico ($26 \text{ g} \cdot \text{min}^{-1} \cdot \text{g}^{-1}$). As velocidades médias de absorção de CO_2 em diferentes temperaturas para a mistura analisada encontram-se descritas na Tabela 4, juntamente com o tempo de saturação de 90% do material. Para as composições contendo um teor de KOH mais elevado, a velocidade de absorção aumenta consideravelmente, podendo ser até 10% mais rápida, mas devido as proporções estequiométricas a eficiência do material é prejudicada.

Tabela 2: Velocidade de absorção e tempo de saturação para 90% do material cerâmico composto por 88,5% de CaO, 0,5% de KOH, 10% de caulim e 1% de alumínio com exposição a um fluxo de CO₂ de 26 g.min⁻¹kg⁻¹ ou grama de material absorvente.

Temperatura (°C)	Velocidade (g. min ⁻¹ kg ⁻¹)	Tempo ~90% (min)
200	1,2	576
300	12,2	57
400	38,6	18
500	49,7	14
600	189,0	4

EXEMPLO 4: Preparação do material absorvente Classe 4: Gesso

As cerâmicas absorventes da classe 4 utilizam como aglomerante o gesso de paris com uma concentração de até 10% (p/p) e pó de alumínio como agente expansivo com uma concentração de até 1%, e o restante da mistura que corresponde aos componentes absorventes é composta por misturas binárias de CaO e La₂O₃ (Fig 13) , de CaO e KOH (Fig 14), de CaO e MgO (Fig 15).

Misturas que apresentam uma quantidade de gesso inferior a 5% perdem a rigidez prejudicando o manuseamento do material. Uma relação inversa entre o teor de alumínio e rigidez pode ser observada, pois o aumento excessivo da quantidade de bolhas na estrutura do material exige uma maior quantidade de agente aglomerante (gesso). Para o processo de absorção de dióxido de carbono, a temperatura de decomposição do carbonato de cálcio na mistura deve ser superior a 750°C. O processo de regeneração do material exige a adição de agente expensor (alumínio), reduzindo assim a concentração do aglomerante e absorvente em aproximadamente 1 a 2% a cada ciclo. Portanto, considerando a concentração mínima do óxido de cálcio e do gesso de paris, cada mistura possibilita a realização de aproximadamente 5 ciclos de absorção/regeneração sem considerável perda de eficiência e resistência mecânica do material. O oxalato de cálcio pode ser utilizado como agente expensor, só que é necessário tratamento térmico, para que através da

decomposição do oxalato em óxido de cálcio, o dióxido de carbono gerado, cause a aeração do material. Nesse processo é necessário que esse dióxido de carbono seja transformado em insumos no processo inicial de preparação da cerâmica.

5 **EXEMPLO 5: Teste da absorção de CO₂**

Para a verificação do processo de absorção utilizou-se um motor de dois tempos de uma motosserra, que utiliza como combustível uma composição contendo 96% de gasolina e 4% de óleo. A cerâmica da classe 2 de composição 88% de CaO, 1% de KOH, 10% de caulim e 2% de alumínio foi colocada em um
10 forno tubular à 500°C, em uma capela com sistema de exaustão. Em seguida o motor foi acionado e a descarga de gases foi direcionada para a entrada do forno de forma a permitir o contato dos gases com a cerâmica na temperatura do forno. Após cerca de 1 hora o forno e o motor foram desligados. O material obtido foi pesado e a partir da diferença de massa em relação à massa original
15 da cerâmica, verificou-se um ganho de massa sendo comprovado uma absorção de 40%, em massa. A análise elementar de carbono e nitrogênio mostrou uma incorporação de massa relacionada a esses elementos de cerca de 45% de carbono proveniente de CO₂ e de menos 1% de nitrogênio proveniente de óxidos nitrogenados.

20 **DESCRIÇÃO DETALHADA DAS FIGURAS**

A **Figura 1** descreve o ciclo de absorção, produção de insumos e recuperação de materiais absorventes. A figura 1 ilustra em linhas gerais o processo cíclico proposto neste pedido de patente para a absorção de gases ácidos e a reutilização destes para a síntese de insumos industriais,
25 regenerando o material absorvente. O esquema inicia com a preparação do material absorvente (101), que é constituído por dois ou mais óxidos de metais alcalinos terrosos ou alcalinos terroso com óxido alcalino, agentes aglomerantes e agente expensor. A cerâmica absorvente é em seguida exposta a um fluxo de gás, a uma temperatura entre 50 e 600°C (110), o material saturado (111) é
30 trocado (112) e analisado (113) para a determinação do tipo de processo que será utilizado em seu processamento (120) gerando para cada composição um ou mais tipos de insumos (121). Durante o processamento do material saturado, a cerâmica absorvente pode ser regenerada (130) através da recomposição e

moldada novamente (140) estando, portanto, preparada para ser reutilizada na absorção de gases ácidos.

A **Figura 2** descreve processos de regeneração de dióxido de carbono absorvido e regeneração do material absorvente. A figura 2 destaca o processo de recuperação dos materiais cerâmicos descritos no presente pedido de patente após a saturação com dióxido de carbono, o que não limita a aplicação dos materiais absorventes, que podem ser empregados para qualquer gás de natureza ácida. Inicialmente, a cerâmica absorvente (200) é exposta ao fluxo de CO₂ que apresenta uma temperatura entre 100 e 600°C. O material saturado (210) pode ser processado por duas vias distintas. A primeira via corresponde à decomposição térmica dos carbonatos formados em uma temperatura aproximada de 800°C (260). Nesta via, o CO₂ (250) liberado é conduzido aos sistemas de processamento de interesse industrial. O dióxido de carbono pode ser armazenado (251) ou transformado em outros produtos como, por exemplo, carbonato (252) e carbamato (253). O fluxo de CO₂, que apresenta elevado teor de concentração, pode ser utilizado para a produção de carbamato de amônio ou carbonatos diversos, tais como carbonato de amônio ou carbonato de sódio. O dióxido de carbono (250) pode também ser regenerado através da reação do material saturado (210) com um ácido (220), tal como ácido nítrico, mas não limitante. A mistura restante formada é alcalinizada com a adição de NaOH (230), fazendo com que os hidróxidos de metais alcalinos terrosos e outros hidróxidos insolúveis sejam precipitados, possibilitando a separação por filtração ou decantação. Em seguida adiciona-se alumínio pulverizado (230) para a realização do processo de expansão da massa. Finalmente, o material é aquecido para remoção do excesso de água (240) e endurecimento do material cerâmico, que está disponível para reiniciar o ciclo de absorção e utilização de dióxido de carbono.

As **Figuras 3, 4, 5 e 6** correspondem às composições das misturas mais adequadas para cada temperatura e que utilizam o MgO como aglomerante e são formadas por CaO e La₂O₃, CaO e KOH, CaO e MgO ou MgO e KOH, respectivamente.

As **Figuras 7, 8 e 9** correspondem às composições das misturas dos absorventes formadas por CaO e La₂O₃, CaO e KOH, CaO e MgO e que são

enrijecidas através da adição de bentonita para as faixas de temperaturas que estas apresentam a capacidade de absorver CO_2 , respectivamente.

5 **As Figuras 10, 11 e 12** mostram as composições de materiais contendo caulim usado para enrijecimento, formados por CaO e La_2O_3 , CaO e KOH ou CaO e MgO , respectivamente. As figuras 13, 14 e 15 correlacionam as composições dos materiais absorventes para misturas contendo até 10% de gesso de paris, para toda a faixa de temperatura que a sua possibilita a utilização desses materiais

REIVINDICAÇÕES

- 1- **MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, caracterizado por compreender agentes absorventes, agente aglomerante, e agente expensor.
- 5 2- **MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, de acordo com a reivindicação 1, caracterizado pelo agente absorvente compreender no mínimo um óxido de metal alcalino terroso, no mínimo um hidróxido de metal alcalino ou no mínimo um óxido de metal de transição.
- 10 3- **MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, de acordo com a reivindicação 1, caracterizado pelo agente aglomerante ser selecionado do grupo compreendendo óxido de magnésio, bentonita, caulim e gesso de paris.
- 15 4- **MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, de acordo com a reivindicação 1, caracterizado pelo agente expensor ser selecionado do grupo compreendendo alumínio metálico e oxalato de cálcio.
- 20 5- **PROCESSO CÍCLICO PARA PREPARAÇÃO E UTILIZAÇÃO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS** caracterizado por compreender a preparação do material absorvente (101), absorção de gases ácidos (110), saturação do material absorvente (111), troca do material absorvente (112), análise do material saturado (113), processamento dos materiais (120), obtenção dos insumos (121), regeneração do material recuperado (130) e recomposição do material absorvente (140).
- 25 6- **PROCESSO CÍCLICO PARA PREPARAÇÃO DE MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, de acordo com a reivindicação 5, caracterizado pela preparação do material compreender as seguintes etapas:
- a) mistura dos componentes: agentes absorventes, agente aglomerante e agente expensor, em meio aquoso;
 - b) repouso da mistura pelo período entre 1 e 5 horas;
 - 30 c) ativação do agente expensor através homogeneização da mistura;

d) aquecimento moderado da mistura a uma temperatura entre 100 e 200 °C, por um período entre 3 e 72 horas;

e) aquecimento rigoroso da mistura na presença de nitrogênio ou na ausência de fluxo de ar, imediatamente após o aquecimento moderado em uma temperatura entre 500 e 800 °C, por um período de aproximadamente 1 hora ou em autoclave a uma temperatura mais baixa, de aproximadamente 200°C.

7- PROCESSO CÍCLICO PARA PREPARAÇÃO DE MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, de acordo com a

reivindicação 6, caracterizado pelo o material poder ser moldado em formatos específicos na etapa posterior à homogeneização, etapa "c", como nos formatos de bloco compacto, bloco vazado (tijolo) ou material pelletizado de gramaturas variadas.

8- PROCESSO CÍCLICO PARA REGENERAÇÃO DO MATERIAL

CERÂMICO, caracterizado por compreender exposição do material cerâmico aos gases ácidos (210) seguido das seguintes etapas:

a) decomposição térmica a uma temperatura aproximada de 800°C (260), recuperação do material absorvente (200), ou

b) tratamento com ácido mineral (220), tratamento básico e separação dos óxidos de metais alcalinos terrosos e outros óxidos insolúveis por filtragem ou decantação seguido da adição de agente expensor (230), aquecimento a temperatura entre 100 e 500°C (240) e recuperação do material absorvente (200).

9- PROCESSO CÍCLICO PARA REGENERAÇÃO DOS GASES ÁCIDOS

ABSORVIDOS E REGENERAÇÃO DO MATERIAL CERÂMICO, de acordo com a etapa da reivindicação 4, caracterizado pela adição de alumínio ou oxalato de cálcio, com uma concentração entre 1 e 2%.

10- PROCESSO CÍCLICO PARA REGENERAÇÃO DOS GASES ÁCIDOS,

caracterizado por compreender exposição do material cerâmico aos gases ácidos (210) seguido das seguintes etapas

a) decomposição térmica a uma temperatura aproximada de 800°C (260), liberação dos gases ácidos regenerados nos sistemas de processamento de interesse industrial (250), armazenamento dos gases ácidos nos sistemas de processamento (251) ou transformação em outros produtos (252) e (253), ou

b) tratamento com ácido mineral (220), liberação dos gases ácidos regenerados nos sistemas de processamento de interesse industrial (250), armazenamento dos gases ácidos nos sistemas de processamento (251) ou transformação em outros produtos (252) e (253).

11- PROCESSO CÍCLICO PARA REGENERAÇÃO DO MATERIAL CERÂMICO E DOS GASES ÁCIDOS, de acordo as reivindicações 8 e 10, caracterizado pelo fluxo do gases ácidos apresentarem uma temperatura entre 50 e 600°C.

12- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, caracterizado por possibilitar a absorção de gases ácidos presentes em fluxos gasosos para purificação.

13- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, caracterizado por possibilitar a absorção de gases ácidos poluentes, em sistemas de exaustão com temperatura do fluido entre 50 e 600°C.

14- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, caracterizado por purificar fluxos de gases de admissão para motores de combustão interna, com o objetivo de aumentar a eficiência do processo de queima de combustíveis.

15- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, caracterizado por absorver os gases ácidos liberados pela queima de combustíveis, em motores de combustão interna, com o objetivo de reduzir a emissão de gases poluentes.

16- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS, de acordo com as reivindicações 12 a 15, caracterizado por purificar fluxos de gases ácidos selecionados do grupo compreendendo CO₂, SO₃, SO₂,

NO, NO₂, que podem ser liberados em processos industriais de produção de coque, sinterização de materiais e laminação.

- 17- USO DO MATERIAL CERÂMICO PARA ABSORÇÃO DE GASES ÁCIDOS**, de acordo com as reivindicações 12 a 15, caracterizado por purificar
- 5 fluxos de gases de admissão que contenham gases ácidos, selecionados do grupo compreendendo CO₂, SO₃, SO₂, NO, NO₂ que podem comprometer equipamentos ou a eficiência de processos em usinas termoeletricas.

FIGURAS

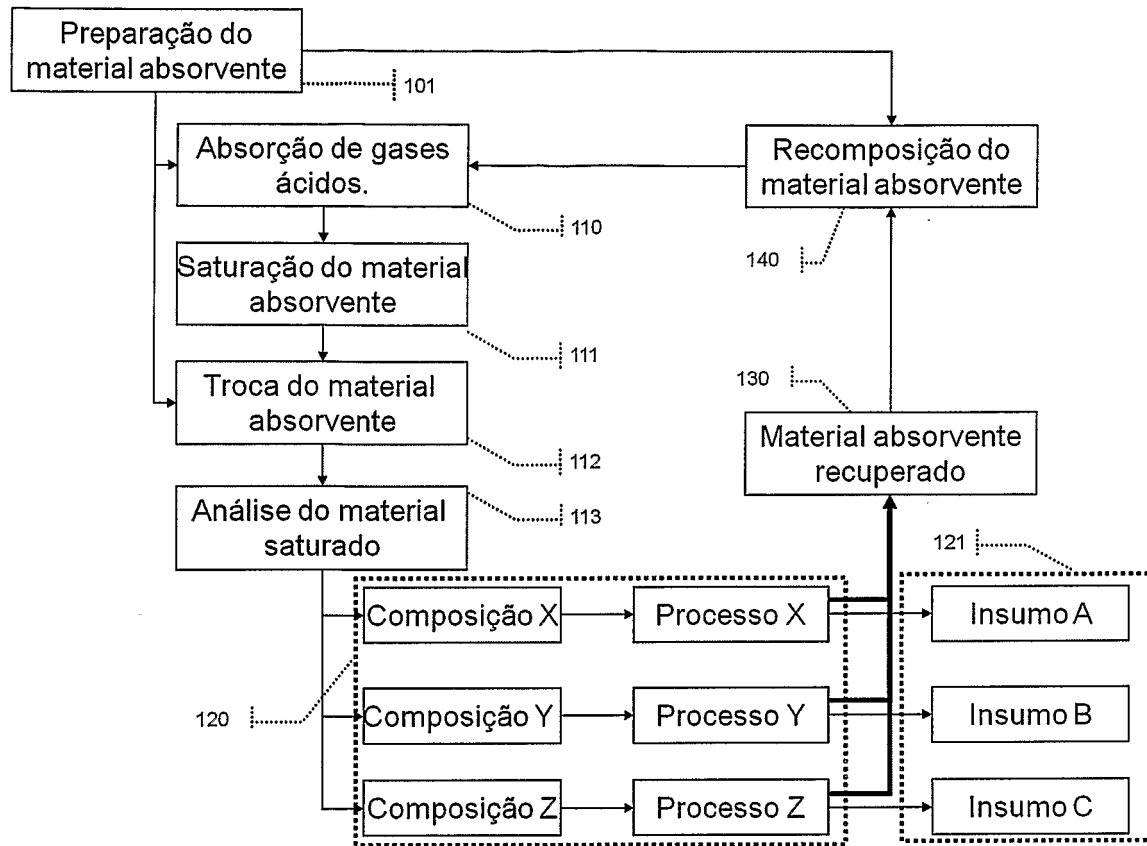


Figura 1

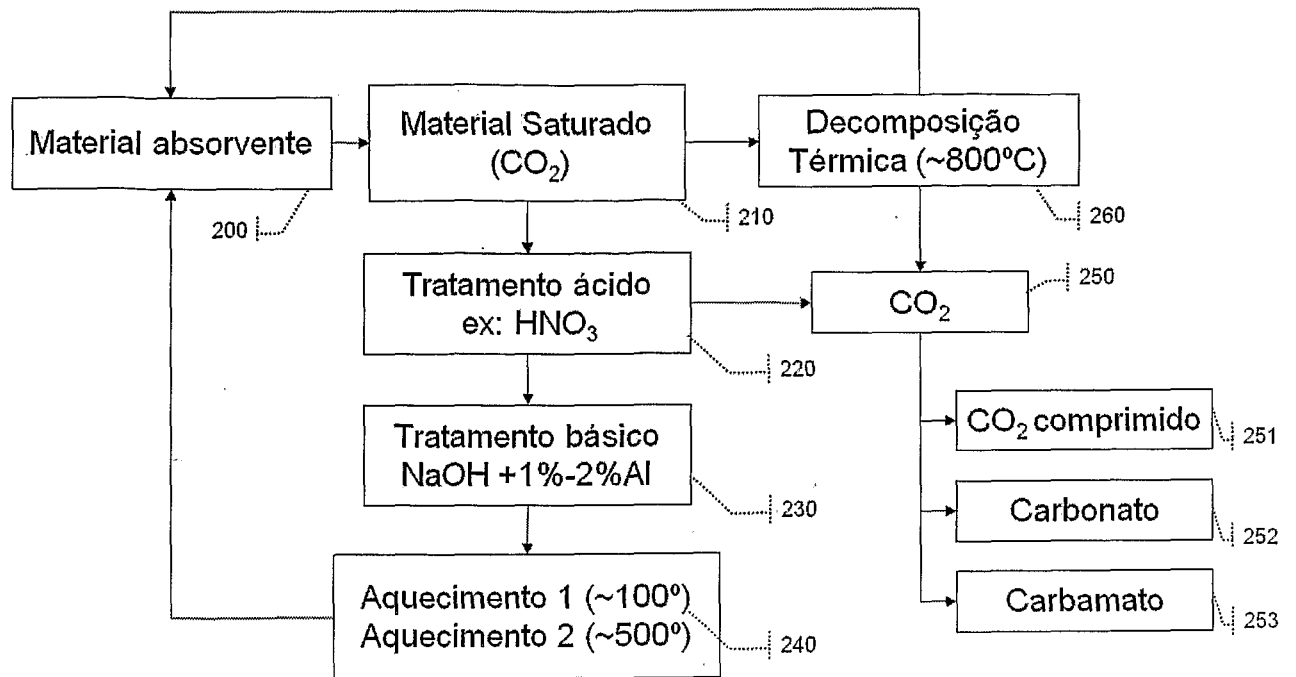


Figura 2

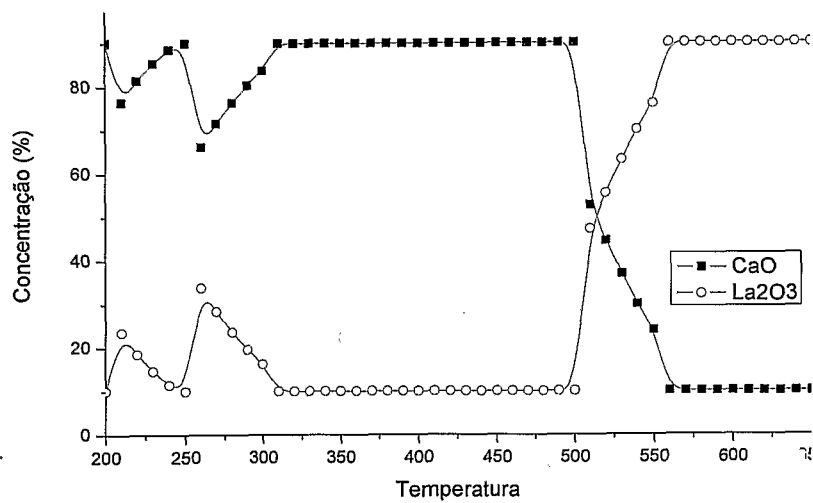


Figura 3

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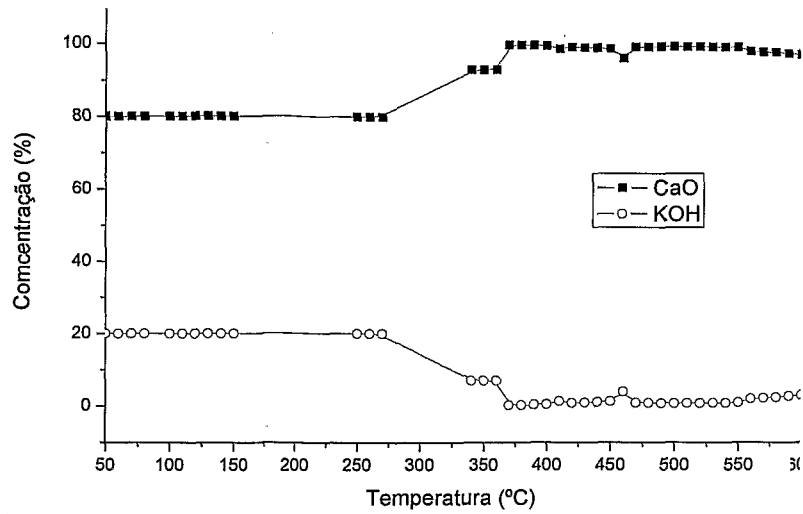


Figura 4

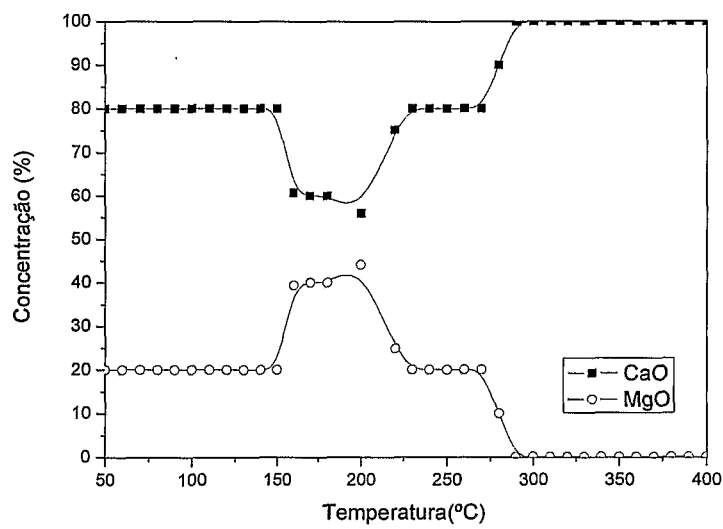


Figura 5

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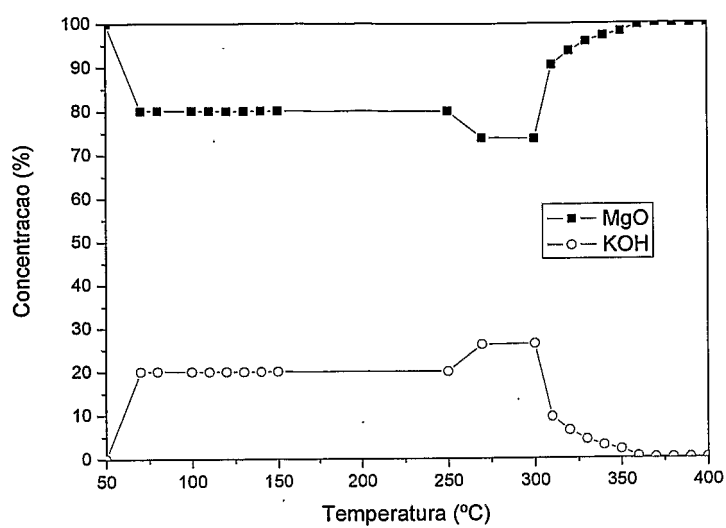


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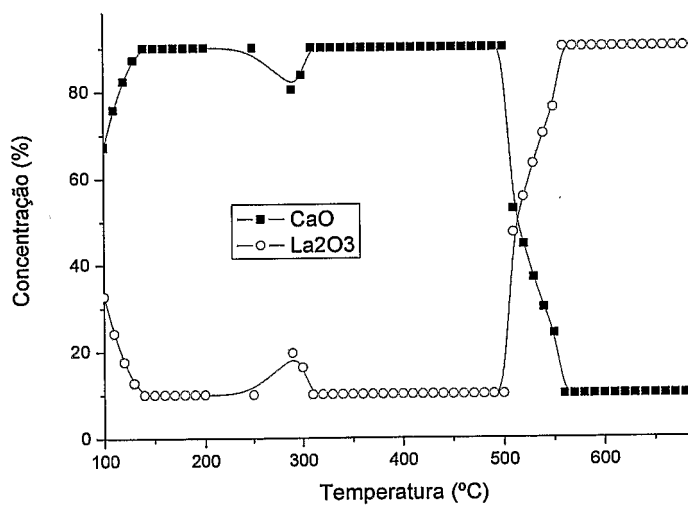


Figura 7

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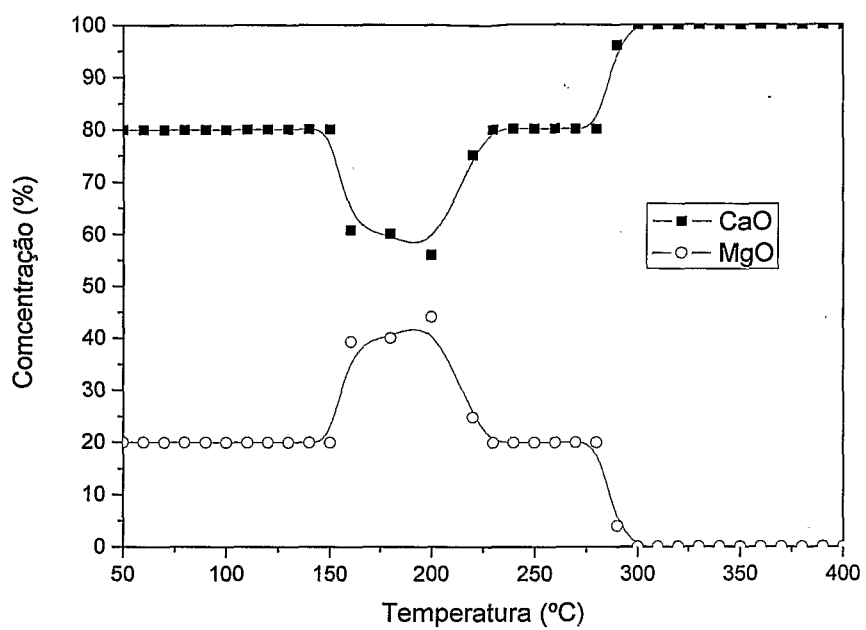


Figura 8

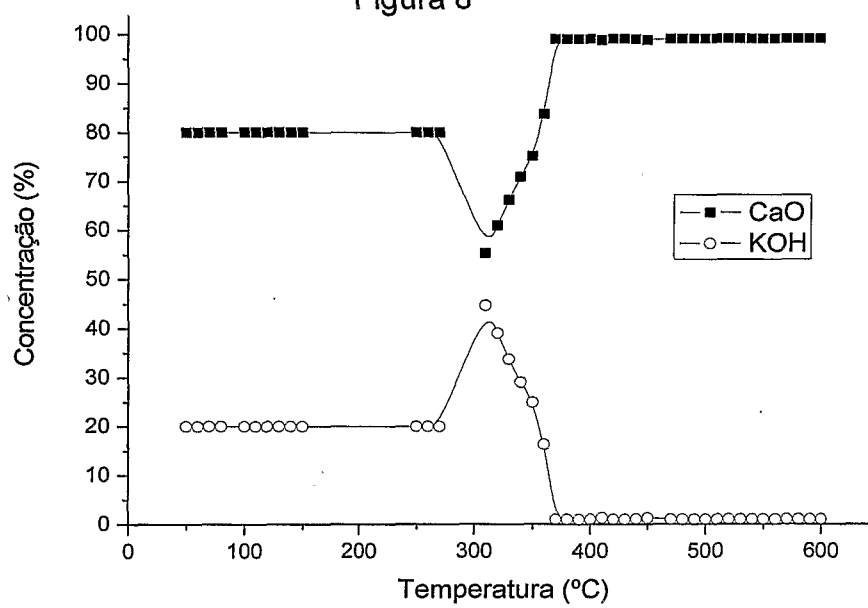


Figura 9

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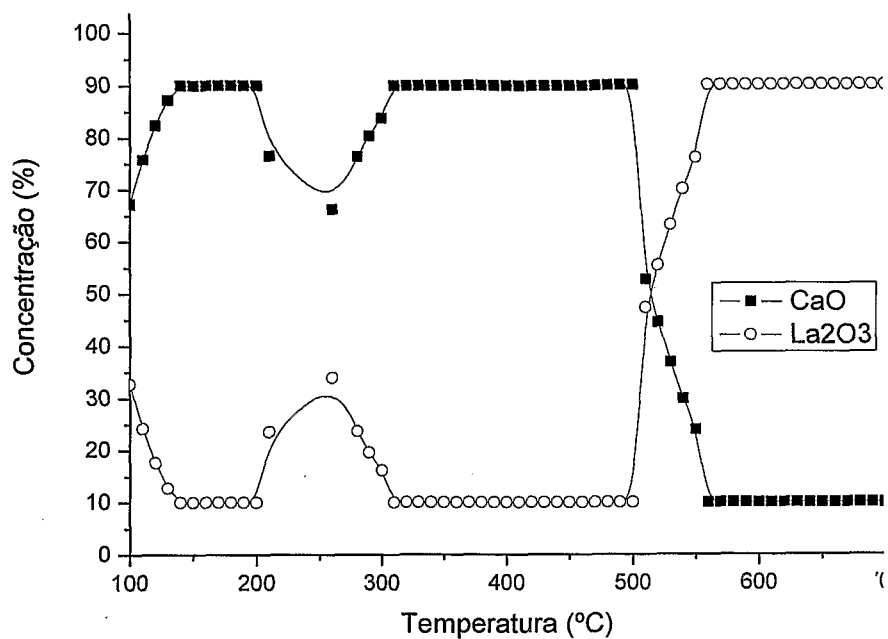


Figura 10

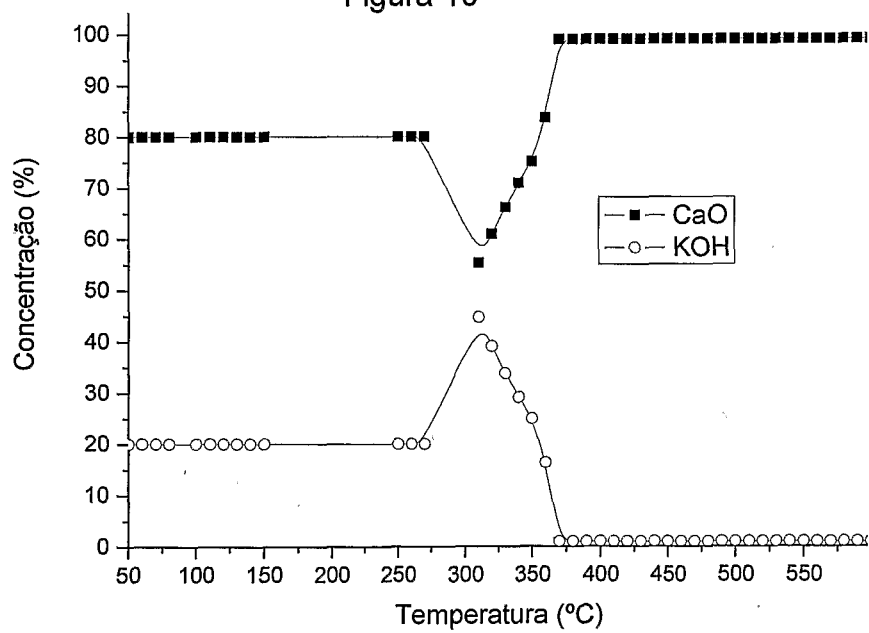


Figura 11

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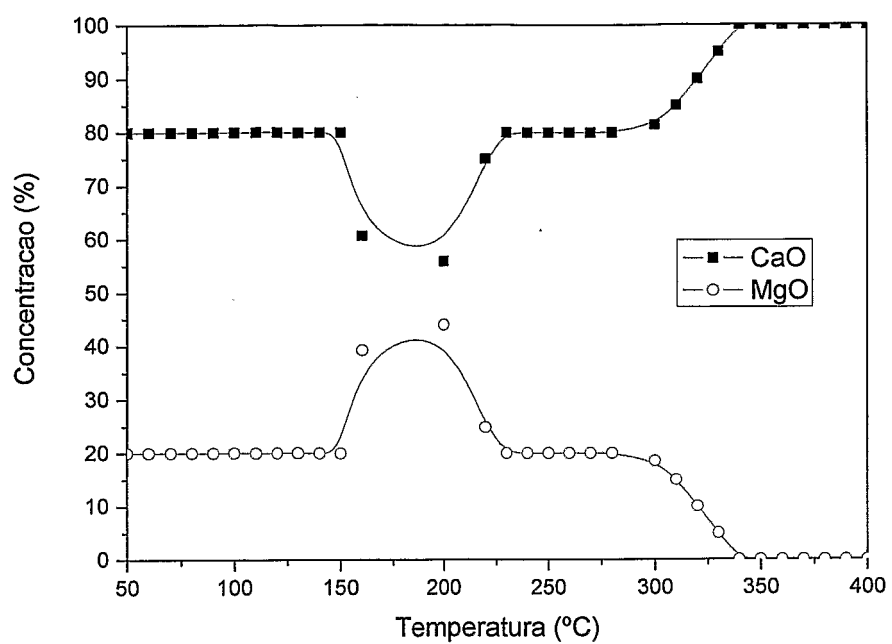


Figura 12

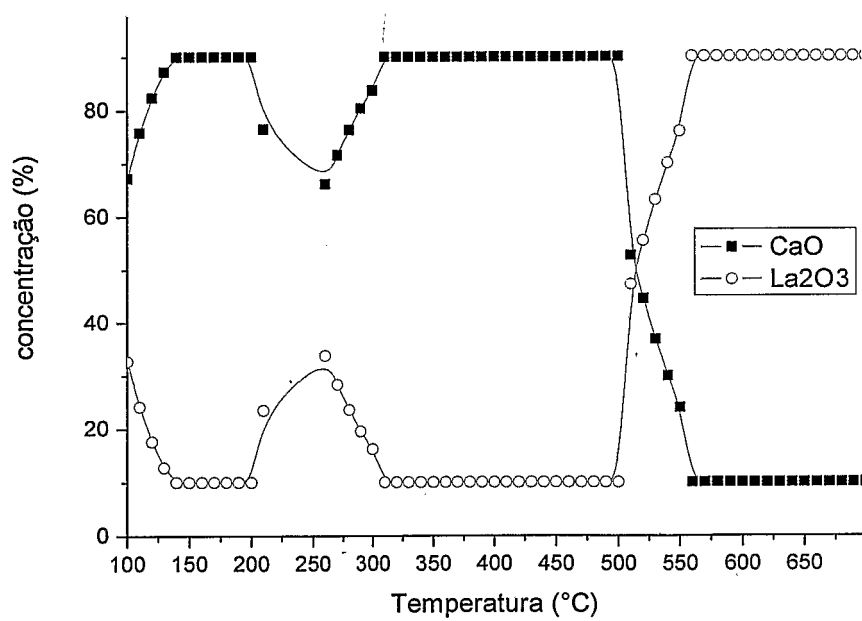


Figura 13

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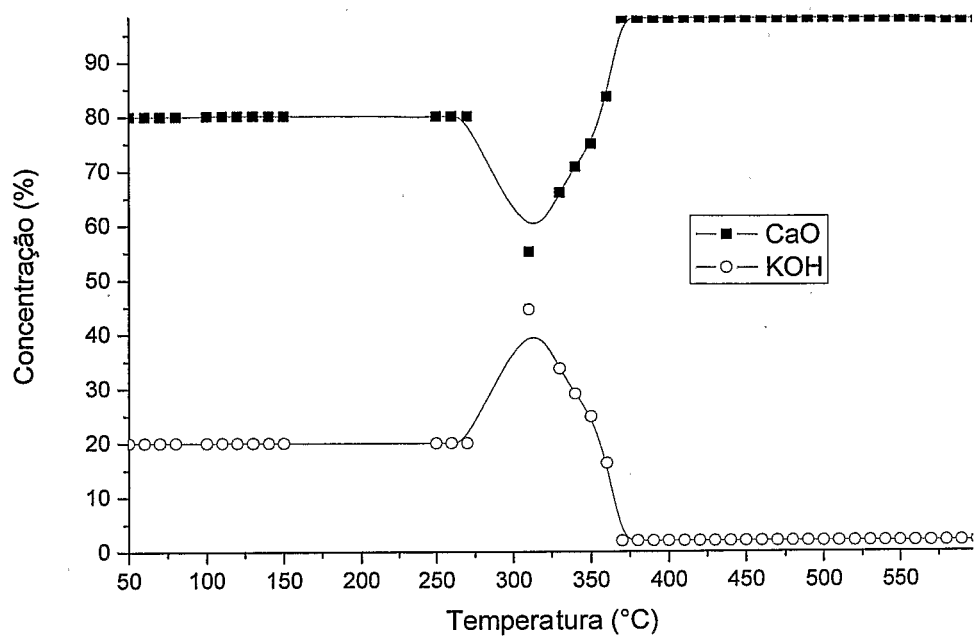


Figura 14

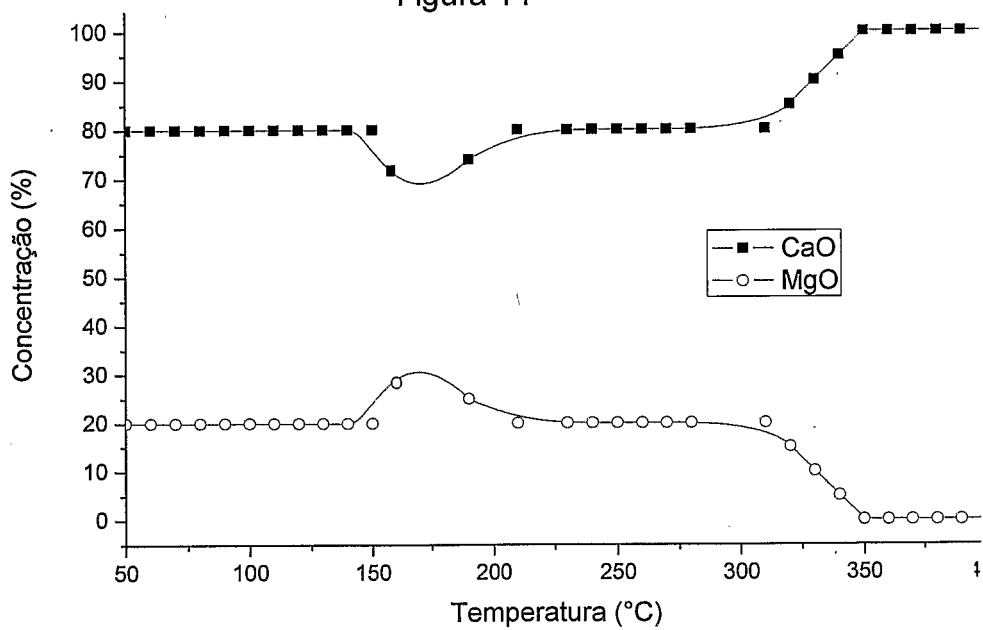


Figura 15