(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
31 May 2012 (31.05.2012)

(10) International Publication Number
WO 2012/070954 A1

(51) International Patent Classification:
B01D 53/14 (2006.01) ***B01D 53/78*** (2006.01)
B01D 53/62 (2006.01)

(21) International Application Number:
PCT/NO2011/000334

(22) International Filing Date:
25 November 2011 (25.11.2011)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20101662 26 November 2010 (26.11.2010) NO

(71) Applicant *(for all designated States except US)*: **UNIVERSITETET FOR MILJØ- OG BIOVITENSKAP** [NO/NO]; Institutt for Matematiske Realfag og Teknologi, P.O. Box 5003, N-1432 Ås (NO).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **OLSEN, Espen** [NO/NO]; Kirkeveien 17, N-1430 Ås (NO).

(74) Agent: BRYN AARFLOT AS; P. O. Box 449 Sentrum, N-0104 Oslo (NO).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *with amended claims (Art. 19(1))*

(54) Title: METHOD FOR REMOVAL OF CARBON DIOXIDE FROM A GAS STREAM

(57) Abstract: Present invention relates to a method for capturing of carbon dioxide from a flue gas by using CaO dissolved in a mixture of NaF and CaF_2 in molten state as the absorption medium.

WO 2012/070954 A1

Method for removal of carbon dioxide from a gas stream

The present invention relates to the capture of carbon dioxide, CO_2, from exhaust gas using calcium oxide dissolved in a salt melt as an absorption medium.

In a conventional heat power plant, coal is oxidized with air in a ratio >> 1. The exhaust gas from a conventional fired boiler contains 10 – 15 % CO_2 and the temperature is 800 °C at the boiler exit. The hot exhaust gas is heat exchanged with water and generates superheated steam under high pressure that is used to drive a turbine which again drives a generator for electrical power. The electrical efficiency is relatively low, about 40 – 60 %. The heated steam is condensed before it once again is heat exchanged with the hot exhaust gases from the combustion process. The condensation process releases considerable heat that can be used for the purpose of remote heating in so called combined heat and power plants (CHP). This increases the total efficiency of a plant to about 70 %.

The most current technology for the cleaning of CO_2 from a heat power plant is based on the absorption of CO_2 in amines. After decompression and cooling in the turbine, the exhaust gases are passed through a large reactor where CO_2 is absorbed in an amine based liquid at 30 – 40 °C. The remaining exhaust gases are released to the atmosphere, but the CO_2 rich amine liquid is fed into another chamber where the temperature is increased to 120 – 130 °C and CO_2 is selectively released. The released gas can then be compressed to a liquid and disposed of at a suitable location. The amine absorbent is cooled to 30 – 40 °C and passed into the absorption chamber where the process starts over again. The temperature exchange of large amounts of absorbent requires a considerable amount of energy and reduces the electrical output from the plant by about 10 %.

A general thermal power conversion process can be represented by the diagram in Figure 2. Heat (Q_H) flows from a reservoir at a high temperature T_H through a machine to a reservoir at a low temperature T_L. Work W is performed along the way while heat Q_L is added at the low temperature reservoir. The efficiency of the process is given by equation (1).

$$\eta = \frac{W}{Q_H} \qquad (1)$$

The theoretical efficiency (Carnot efficiency) for a thermal power conversion process is generally given in equation (2) where T_H and T_L are low and high temperatures, respectively, in the power conversion process.

$$\eta = \frac{T_H - T_L}{T_H} \qquad (2)$$

This represents a fundamental limit for the efficiency of thermal processes. In general, it is preferable to have as large temperature differences as possible in order to increase efficiency.

When recovering energy from the temperature exchange from 130 °C to 40 °C in an amine process, the theoretical output according to equation (4) is 66.9 %. In practice, it is far lower, and energy from the recovery process is present as relative low quality heat energy which can primarily only be used for heating. A gas power plant with amine cleaning is presented in Figure 3.

RU2229335 C1 relates to an absorption medium for CO_2 that is a mixture of calcium oxide and a eutectic mixture of alkali metal carbonates manufactured in the form of grains.

JP11028331 A discloses electrochemical separation of CO_2, where CO_2 is converted to CO_3 at the cathode by an electrochemical reaction.

JP 10085553 discloses separation of CO_2 by passing the exhaust gas through a membrane where the fibres consist of a composite oxide that creates CO_2 by a chemical reaction with CO_2 and an oxide.

US2005036932 discloses a method for absorbing and removing CO_2 from an exhaust gas. The exhaust gas is blown through an agglomerate of solid particles containing CaO and/or $Ca(OH)_2$ such that CO_2 in the exhaust gas is converted to $CaCO_3$.

Terasaka et al. (Chem. Eng. Technol. 2006, 29 No 9, pages 1118-1121) has disclosed a process where CO_2 is absorbed using solid particulate lithium silicate ($LiSiO_4$) in a slurry of molten salts as the working medium. Li_2CO_3 and Li_2SiO_3 are formed and are present as solid particles in the slurry.

Current technology discloses several different methods for the capture of CO_2. The disadvantages to these include primarily the size of the treatment plants and low energy efficiency in the power conversion process.

It is an object of the present invention to obtain a method for cleaning CO_2 from exhaust gases from combustion plants, where the method will provide improved efficiency and power quality for energy recovery from the cleaning process. In addition, it is desirable to improve the efficiency of CO_2 cleaning with using faster chemical reactions so that the physical size of the cleaning plant can be reduced.

The present invention provides a method for the removal of carbon dioxide from a gas stream, where the gas stream in a first step is brought in contact with an absorption medium in molten state wherein the medium comprises 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture, and that reacts with the carbon dioxide to form a soluble calcium carbonate. The method is performed at a pressure close to atmospheric pressure above the absorption medium.

Further the invention relates to the use of an absorption medium comprising 99-50 % by weight of a molten salt being a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture for the removal of carbon dioxide from a gas stream.

The invention also provides an absorption medium for the removal of carbon dioxide from a gas stream, where the absorption medium comprising 99-50 % by weight of a molten salt being a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture.

Figures:

Figure 1 is a schematic illustration of a conventional heating power plant (B. Sørensen).

Figure 2 is a schematic illustration of a general power conversion process.

Figure 3 is a schematic illustration of a gas power plant with an amine cleaning plant from SINTEF.

Figure 4 is a graph illustrating the Gibbs free energy for reaction (5). Positive values indicate that the reaction progresses toward the left. Negative values indicate that the reaction progresses toward the right.

Figure 5 is a schematic diagram of high temperature molten salt absorption of CO_2 from a gas power plant.

Figure 6: Phase diagram CaF_2 – NaF

Figure 7: Sketch of experimental apparatus (cell)

Figure 8: Presentation of results from absorption of CO_2 by use of the inventive method.

Figure 9: Presentation of results from the desorption process

Figure 10: Diagram showing absorption and subsequent desorption of CO_2 in a molten salt

Molten salts are used in the chemical process industry in different applications. Worth mentioning are electrolytes in electrolytic processes, as catalytic media in pyrolytic processes and as electrolytes in batteries and photoelectrochemical solar panels. In general, molten salts consist of metal-anion compounds with varying compositions. These in themselves are thermodynamically very stabile, while also being efficient solvents for other compounds and elements. Some molten salts have a degree of solvency for carbon in the form of CO_2. This is particularly applicable for chlorides such as $M\text{-}Cl_x$, fluorides such as $M\text{-}F_x$ and nitrates such as $M\text{-}(NO_3)_y$, where M is a metal with a valency of x or y/2.

In general, oxides will be soluble in molten salts with opposite Lewis acid-base characteristics so that acidic melts dissolve basic oxides and vice versa. A good example of this is $CaCl_2$ which in itself has a weakly acidic character. This results in basic oxides (CaO, MgO) and to a certain extent amphoteric oxides being easily dissolved, while acidic oxides (SiO_2, TiO_2) are only minimally dissolved. Basic oxides have an affinity for CO_2 during the formation of carbonates according to the equation (3)

$$CaO + CO_2 \rightleftharpoons CaCO_3 \qquad \Delta G^0_{300K}=-130 \text{ kJ/mol} \qquad (3)$$

Similarly to calcium oxide, calcium carbonate has basic properties and will generally dissolve in acidic melts. This is, however, not universally valid since both CaO and $CaCO_3$ will also dissolve in fluorides such as CaF_2 which exhibit basic properties. Calcium carbonate is very stable at room temperature, but will decompose to CaO and CO_2 according to the equation (4) at temperatures above 850 – 900 °C. Table 1 shows ΔG for reaction (3) as a function of temperature. This is the opposite reaction of (4) so that the same numbers apply for (4), but with opposite sign.

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (4)$$

Table 1: Gibbs free energy for reaction (5) as a function of temperature.

Temp (°C)	ΔG (kJ/mol)
500.000	-56.640
600.000	-41.695
700.000	-26.945
800.000	-12.385
900.000	1.986
1000.000	16.169
1100.000	30.164
1200.000	43.973
1300.000	57.595
1400.000	69.429
1500.000	80.317

By taking advantage of the affinity CaO has for CO_2, the reaction (3) and (4) can be used for capture of said gas from a diluted gas mixture, e.g. from a coal power plant, by passing the gas mixture through molten salts with dissolved CaO which then will draw carbon dioxide from the gas mixture and form $CaCO_3$. The temperature of molten salts is normally in the area of 600 – 1500 °C and the high temperature, combined with the catalytic properties of the molten salts, provides for very efficient capture.

The Gibbs free energy ΔG of reaction (3) and (4) for the other earth alkali metal oxides is calculated using HSC Thermodynamic Software Tool, Outotech 2008.

Figure 4 shows that the free energy according to (4) for the different earth alkali metal oxides changes its sign at higher temperatures as we move further down the periodic system. This can be taken advantage of by using the heavier oxides for absorption in combustion processes where the exhaust gas temperature is high. It is advantageous to have a large driving force (large, negative ΔG) to ensure a fast processes. Meanwhile, the speed of the processes normally increases with increasing temperature. This leads to opposite effects for the absorption of CO_2 in molten salts, so optimal working conditions must be found experimentally in each case. When oxide and corresponding carbonate are present and dissolved in the molten salts, they will constitute a different medium and environment than when they are present in free form in unit activity as predicted in (4), but qualitatively the behavior will be similar for the different cations. Similar calculations for the alkali metal oxides show that these are more stable so that the sign in reaction (4) will not change at the given operating temperature. This applies to the conditions that the calculations are performed at (STP, unit activity, solid phase) and is not necessarily representative when the reactants are dissolved in the molten salts. Under these conditions, the stability of the compounds will be lower so that alkali metal oxides/carbonates also function as active compounds in the invention.

The CO_2–solubility in the gaseous state in molten salts is a function of temperature in that the solubility decreases with increasing temperature T. This is disclosed to a certain extent in E. Saido, et al., J Chem Eng, Data, 25, (1), 1980, pages 45-47. The solubility of the gaseous CO_2 is in the area of 0.1 – 1 % and can lead to a reduction in process efficiency during the formation and decomposition of $CaCO_3$.

Solid phase reactions are not included in the present invention since the reactants are present as dissolved complex ions in the stated molten salts. This results in significantly faster kinetics than in the prior art and there is therefore no need for a slurry as the solution can be held in a liquid state. Instead of absorbing CO_2 from the combustion gases in the low temperature zone after heat exchange with steam, this can be conducted prior to cooling of the combustion gases. Immediately after combustion, the gases have a temperature in the area of 800 – 1400 °C. In a coal power plant the gases are present at approximately atmospheric pressure and withdrawal of energy occurs in a conventional steam boiler where water is heated to approximately the same temperature as the exhaust gases for driving the steam turbine which in turn drives the electric generator (Figure 1). There is no reason for CO_2 to not be absorbed from the exhaust gases in a hot and/or pressurized condition. Molten salts, such as those presented above, have a melting point generally in the area of 600 – 1412 °C, which falls within the temperature range of the combustion process. Such an absorption process can in principle be carried out as an amine process, but at higher process temperatures. The absorption temperature will be in the range of 600 - 1600 °C. It is assumed that the increased temperature will result in faster process kinetics so that a plant of this type can be made physically smaller than an amine absorption plant which is physically very large. A plant of this type is presented in Figure 5. In a gas power plant, the combustion gases will be highly pressurized before the turbine, which provides an additional increase in the efficiency of this process if it is placed here, since the partial pressure of CO_2 in the gas mixture will be significantly higher than at atmospheric pressure (10-20 atm).

According to the invention hot exhaust gases are passed through molten salts consisting of NaF and CaF_2 at approximately 850 °C, where CO_2 is absorbed by the dissolved CaO in the molten salts in a chamber during the formation of $CaCO_3$. The melt, which has a high $CaCO_3$ content, is then passed to a desorption chamber and heated to approximately 950°C in order to release the gas. This can be explained theoretically by equation (5) which moves toward the left at $T > 850$ °C when $\Delta G > 0$ (see Table 1).

$$CaO(diss, CaCl_2) + CO_2(g) \rightleftharpoons CaCO_3(diss, CaCl_2) \qquad (5)$$

The treated exhaust gases and CO_2 then undergo heat exchange with water in separate circuits in order to generate high temperature steam to drive a steam turbine which, in turn, drives an electric generator. The molten salts containing dissolved and regenerated CaO, are cooled to 800 °C prior to reintroduction to the absorption chamber. In this process the melt undergoes heat exchange with steam which again will drive a turbine for the generation of electric power – preferably the same that is powered by steam generated from the hot exhaust gases. The advantage of cleaning the gas while it is at a high temperature is that it will provide a higher electrical efficiency from the total power conversion process. The theoretical Carnot efficiency (see equation 2) in such a process for the recovery of process heat from the cooling of molten salts from

950 °C to 800 °C in the absorption plant, is 95 %, if we assume that T_L is about 40 °C after extraction of power from the cooling medium (and condensation in the case of steam) to electrical power, along with a T_H of about 800 °C. In addition, this will generate high quality electrical power instead of low quality water borne heat.

Alternately, the change in pressure between the absorption and desorption chambers can, in principle, function in the same way as a change in temperature. In a gas power plant, a greater proportion of the power in the fuel is related to the hydrogen content of the gas and therefore a third method exists for the removal of CO_2 released to the atmosphere, that is electrochemically removal of the carbon from the dissolved carbonate in the molten salts in the desorption chamber. In this case, elementary carbon is generated which can be removed from the process path and be disposed of. This is an alternative to the precombustion reformation of natural gas to carbon (carbon black) and hydrogen prior to combustion of the hydrogen.

An immediate challenge with the concept presented above, is that any water that is present in the combustion gas to be cleaned, can lead to hydrolysis of some molten salts, primarily chlorides, to oxyhydrochlorides. This can be avoided by using melts that are not subject to this problem, preferably basic fluorides, or a continuous regeneration process can be run where some of the melt is continuously withdrawn for treatment.

The salt melt used in the method according to present invention comprises NaF and CaF_2 wherein the content of NaF preferably is within the range of from 45 to 95 % by mole, preferred from 55 to 85 % by mole, more preferred from 60-75 % by mole.

The amount of CaO dissolved in the salt mixture is preferably within the range from 1-50 % by weight, preferred from 5-35 % by weight, more preferred from 10-25 % by weight.

The melting point for the absorption medium (the mixture of salt + oxide/carbonate) must be below the temperature where metal oxide and metal carbonate alternate being the stable phases. This appears from Table 1 and Figure 4. It is important controlling the melting point of the mixture. In the present method, the temperature in the reaction chamber will preferably be in the range from 700 to 1200°C. The absolute pressure in the reaction chamber will be in the range from 0.5 to 200 bar.

Experimental and results

A salt mixture consisting of 65 % by mole of NaF and 35 % by mole of CaF_2 was prepared by melting together substances of chemical grade (Merck) at 900°C in a Ni-crucible. This is close to the eutectic minimum of the system NaF-CaF_2 shown in Figure 6. The mixture was after solidification crushed into smaller pieces for preparation for the electrolyte. Subsequently, 850 grams of the salt mixture were added 150 grams of CaO and filled in a Ni-crucible. The mixture was melted at 850°C in a closed cell shown in Figure 7. The column height of the molten phase was ca. 20 cm. First a simulated flue gas consisting of 22 % by weight of CO_2 + 78 % by weight of N_2 (200 ml/min) was fed into the area above the molten phase through a tube of nickel centrally placed, and then out through a feed tube made of stainless steel. The gas composition was monitored using a high sensitivity FTIR gas analyzer (Thermo Nicolet 6700) suitable for very accurate measurements of CO_2. Because the cell had a volume for analysis of ca. 200 ml, and together with the volume above the molten salt , stable analysis were obtain after a certain time when the total volume was filled with the gas from the cell. Consequently, the pressure in the cell will be approximately atmospheric pressure above the molten mixture, but a certain overpressure will exist in the bottom of the cell where gas is bubbled through the melt. The overpressure can be estimated to ca. 0.03 atm and is due to the weight of the 20 cm column of molten salts containing CaO having a density of ca. 2.2 g/cm^3. When stable values corresponding to the specifications of the gas mixture were obtained (22 % by weight CO_2) the central gas feed tube was immersed into the molten mixture to 1 cm above the bottom, while gas continuously was supplied. The gas composition was monitored and after a short time it was observed that the content of CO_2 decreased. The content of CO_2 was decreased to ca. 500 ppm. Then the Ni-tube was raised above the molten mixture again and the gas composition was increasing until stabilizing at 22 % by weight of CO_2. The cell was left in hot condition over night without gas stream.

The next day the gas supply was switched to argon (Ar 5.0) and 250 ml/min was supplied through the Ni tube again immersed into the molten mixture. A certain initial content of CO_2 was measured, -something which probably was due to residues from the day before, which still were present in pipes/tubes and analysis volume. However, this decreased rapidly and when the content of CO_2 was measured below 100 ppm, the temperature of the furnace control was increased to 950°C. The temperature in the area above the molten mixture was monitored and when this raised above ca. 900 °C CO_2 was again observed in the gas stream now consisting of Ar. When the temperature increased to 950°C, the content of CO_2 increased and reached a maximum at ca. 0.3% for then again decreasing. This was explained in that CO_2 now was released, the reaction [9] went towards left due to changed thermodynamics according to Table 1 and Figure 4.

The experimental parameters are summarized below.

Melt: 35% CaF_2/65% NaF added 15% CaO.

Absorption temperature: 850°C, Desorption temperature: 950°C.

Pressure: Close to atmospheric pressure, estimated overpressure inlet 0.03 bar.

Gas composition: Absorption – 22% CO_2 residue N_2,

Desorption 100% Ar (5.0). Purity >99.995%.

Further tests have been performed using simulated flue gas with different contents of CO_2 in N_2 (0-100%). Figure 8 shows the absorption of CO_2 from a simulated flue gas (35% CO_2) in the reactor depicted in Figure 4. The N_2 flow rate is ca. 0.5 L/min and the CO_2 flow rate is ca. 0.13 L/min. The composition of the absorption medium is the same as described above. The absorption starts after ca. 40 minutes. The absorption is extremely rapid reaching 99.98% efficiency. The temperature increase observed is due to the exothermic reaction. Figure 9 shows the desorption of CO_2 into a flow of pure N_2 (0.11 Nl/min) from $CaCO_3$ dissolved in the molten salt contained in the reactor. It is observed that the desorption at first is very rapid, and then slows down. In Figure 10, both the absorption and the subsequent desorption of CO_2 are shown. In this case, the N_2 gas flow is 0,5 Nl/min and the CO_2 flow rate is ca. 0.13 L/min. Lower content in the gas during desorption compared with Figure 9 is due to higher flow (5 times) of N_2.

Further tests have been made with different content of CaO, varying from 5 to 20 % by weight. The absorption of CO_2 increases with increasing content of CaO.

CLAIMS

1. A method for the removal of carbon dioxide from a gas stream, **characterized in** that the gas stream in a first step is brought in contact with an absorption medium in molted state, wherein said medium comprises 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture, and that reacts with the carbon dioxide to form a soluble calcium carbonate, the method is performed at a pressure close to atmospheric pressure above the absorption medium.

2. The method according to claim 1, wherein the mixture of NaF and CaF_2 comprises 45-95 % by mole of NaF.

3. The method according to any of the claims 1 to 2, wherein the absorption medium in the next step is heated above the melting point and releases CaO and CO_2.

4. The method according to any of the claims 1 to 3, wherein the absolute pressure in the reaction chamber is within the range 0.5 to 200 bar.

5. The method according to any of claims 1 to 4, wherein the temperature in the reaction chamber is within the range 700 to 1200°C.

6. Use of an absorption medium comprising 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture for the removal of carbon dioxide from a gas stream.

7. Absorption medium for the removal of carbon dioxide from a gas stream, **characterized in** that it comprises 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture.

8. Absorption medium according to claim 7, where the mixture of NaF and CaF_2 comprises 45-95 % by mole of NaF.

AMENDED CLAIMS
received by the International Bureau on 20 March 2012 (20.03.2012)

1. A method for the removal of carbon dioxide from a gas stream, **characterized in** that the gas stream in a first step is brought in contact with an absorption medium in molten state, wherein said medium comprises 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture, and that reacts with the carbon dioxide to form a soluble calcium carbonate, the method is performed at a pressure close to atmospheric pressure above the absorption medium.

2. The method according to claim 1, wherein the mixture of NaF and CaF_2 comprises 45-95 % by mole of NaF.

3. The method according to any of the claims 1 to 2, wherein the absorption medium in the next step is heated above the melting point and releases CaO and CO_2.

4. The method according to any of the claims 1 to 3, wherein the absolute pressure in the reaction chamber is within the range 0.5 to 200 bar.

5. The method according to any of claims 1 to 4, wherein the temperature in the reaction chamber is within the range 700 to 1200°C.

6. Use of an absorption medium in molten state, comprising 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture for the removal of carbon dioxide from a gas stream.

7. Absorption medium in molten state for the removal of carbon dioxide from a gas stream, **characterized in** that it comprises 99-50 % by weight of a mixture of NaF and CaF_2 and 1-50 % by weight of CaO dissolved in the mixture.

8. Absorption medium according to claim 7, where the mixture of NaF and CaF_2 comprises 45-95 % by mole of NaF.

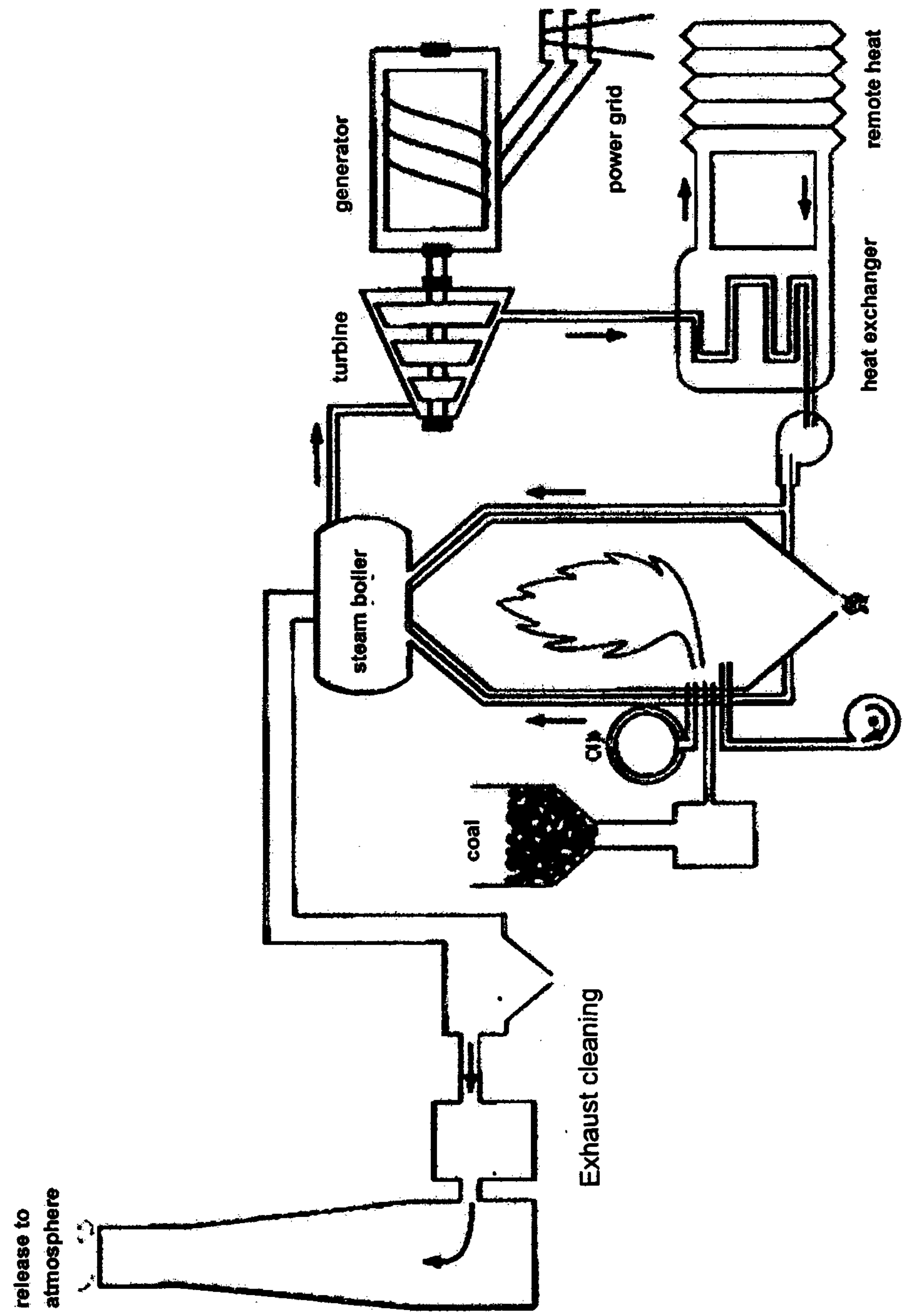
generator
power grid
remote heat
heat exchanger
turbine
steam boiler
air
coal
Exhaust cleaning
release to atmosphere

Figure 1

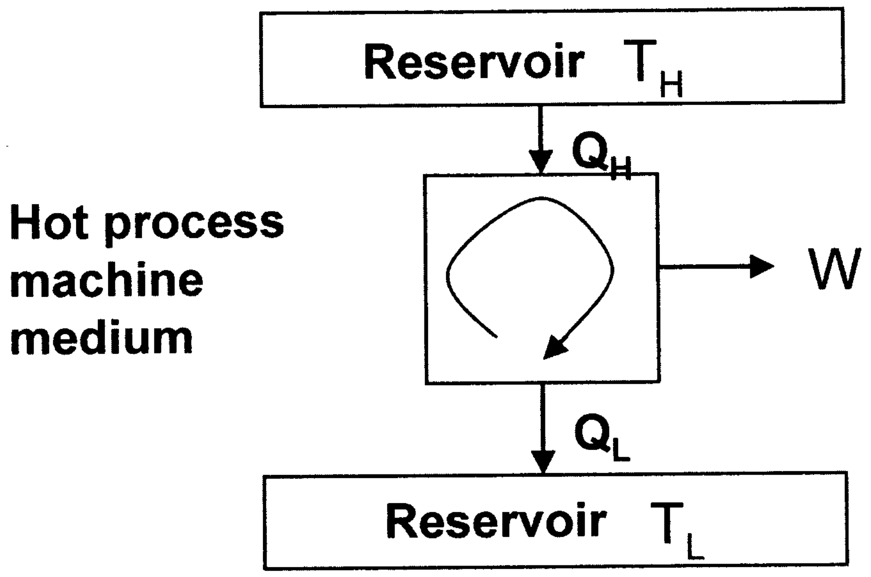
Reservoir T_H
Q_H
Hot process
machine
medium
W
Q_L
Reservoir T_L

Figure 2

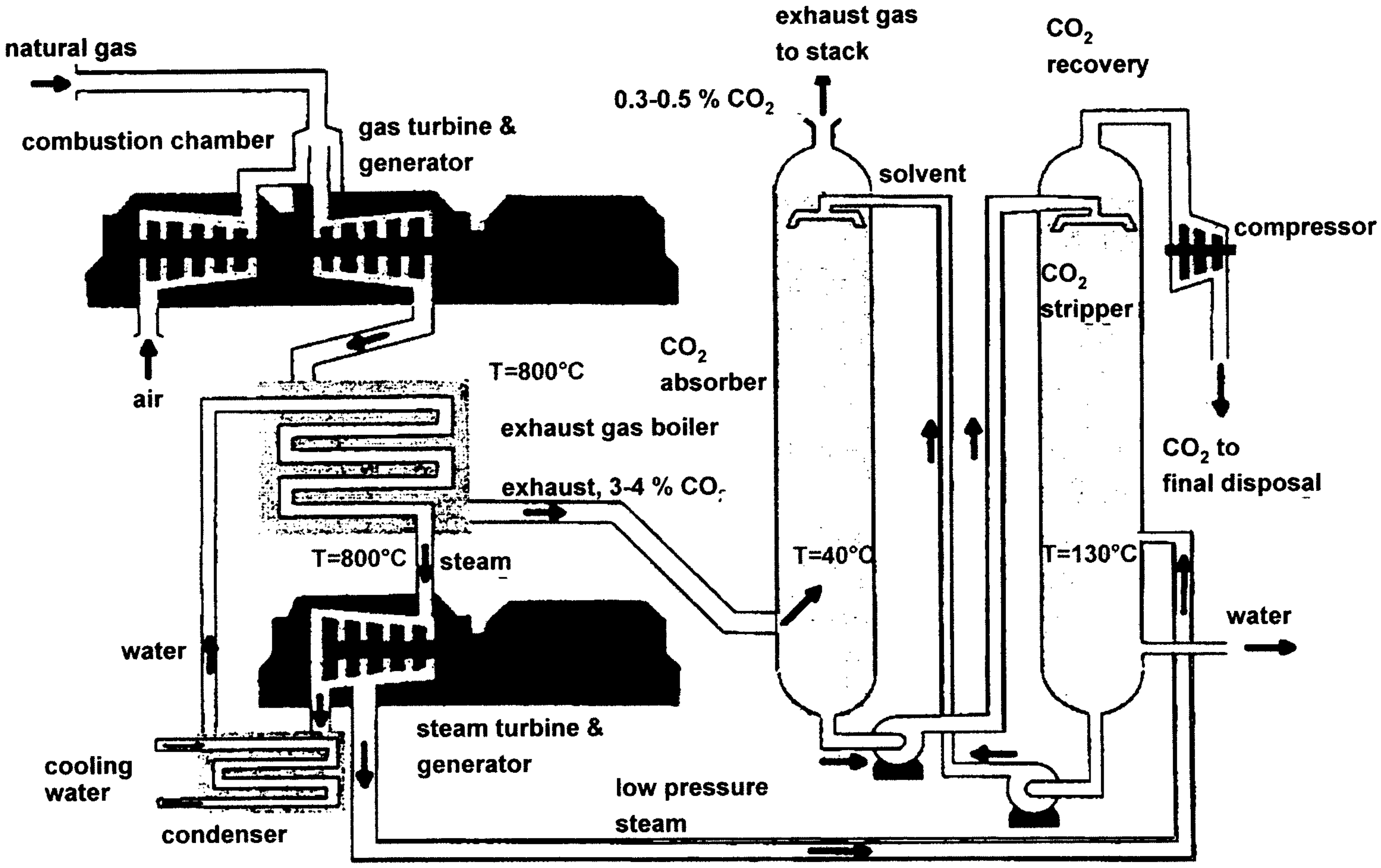
natural gas
combustion chamber
gas turbine &
generator
air
T=800°C
exhaust gas boiler
exhaust, 3-4 % CO2
T=800°C
steam
water
cooling
water
condenser
steam turbine &
generator
low pressure
steam
exhaust gas
to stack
0.3-0.5 % CO2
solvent
CO2
absorber
T=40°C
CO2
recovery
compressor
CO2
stripper
CO2 to
final disposal
T=130°C
water

Figure 3

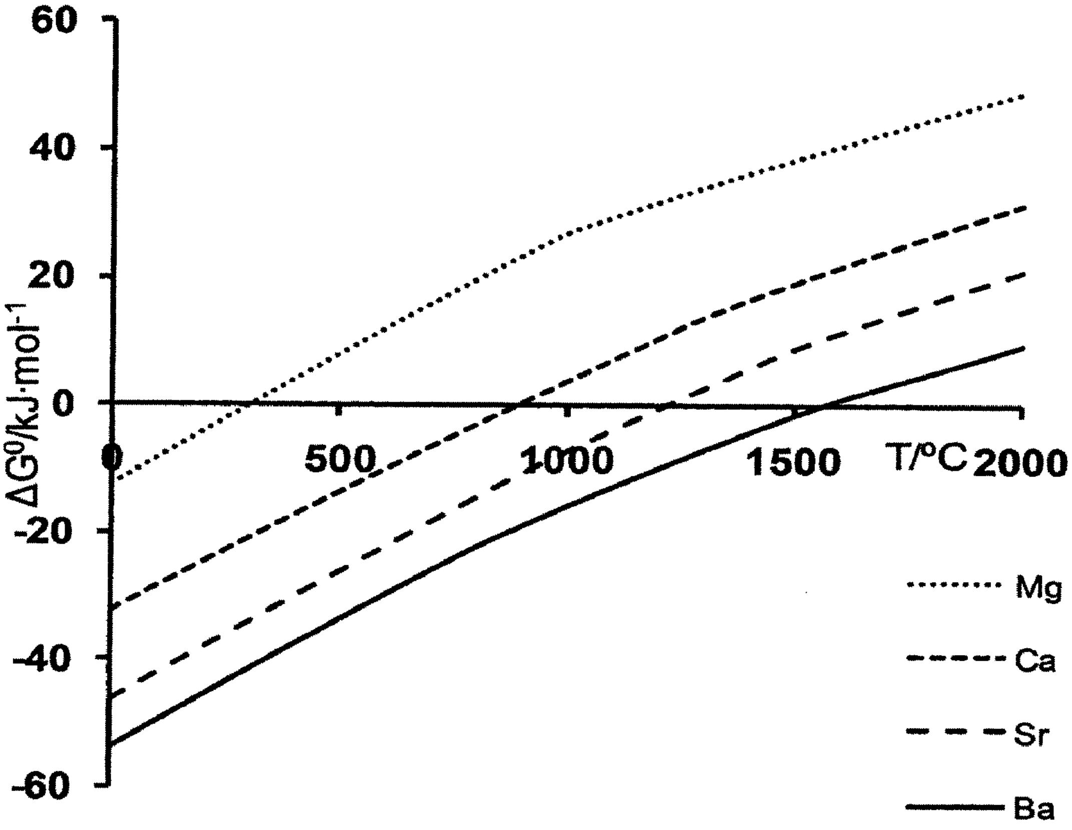

Figure 4

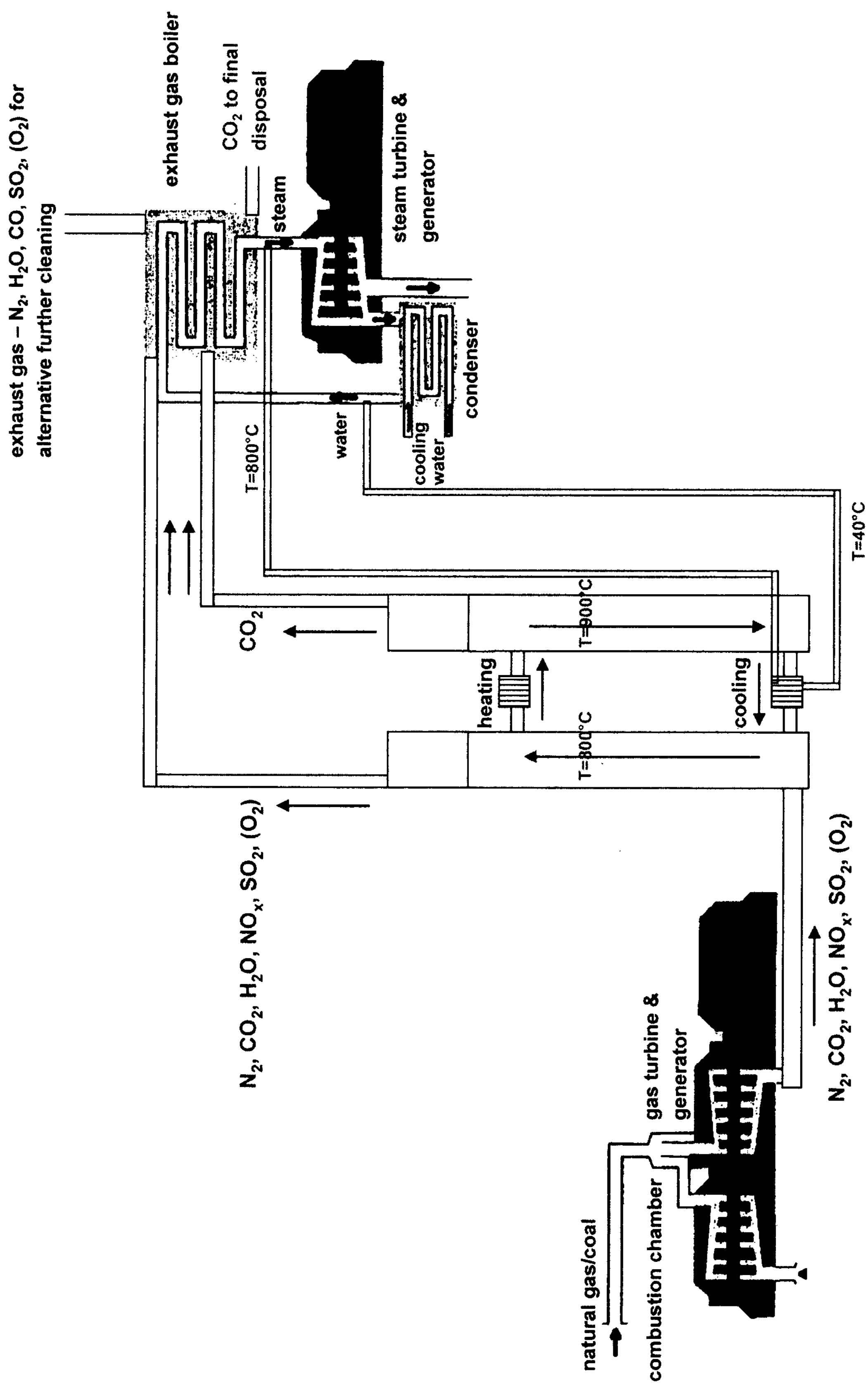
exhaust gas – N_2, H_2O, CO, SO_2, (O_2) for alternative further cleaning
exhaust gas boiler
CO_2 to final disposal
steam
steam turbine & generator
condenser
cooling water
water
T=800°C
T=40°C
CO_2
T=900°C
heating
cooling
T=800°C
N_2, CO_2, H_2O, NO_x, SO_2, (O_2)
N_2, CO_2, H_2O, NO_x, SO_2, (O_2)
gas turbine & generator
combustion chamber
natural gas/coal

Figure 5

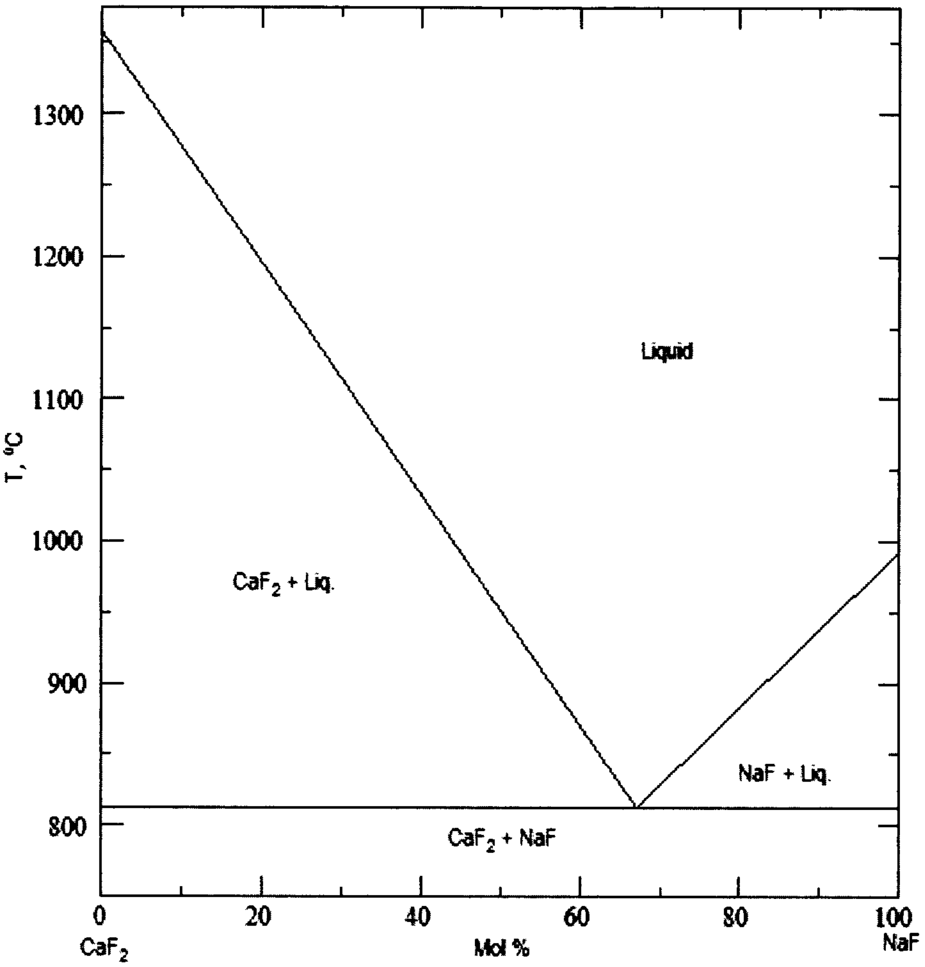
1300
1200
1100
1000
900
800
T, °C
Liquid
CaF_2 + Liq.
NaF + Liq.
CaF_2 + NaF
0
20
40
60
80
100
CaF_2
Mol %
NaF

Figure 6

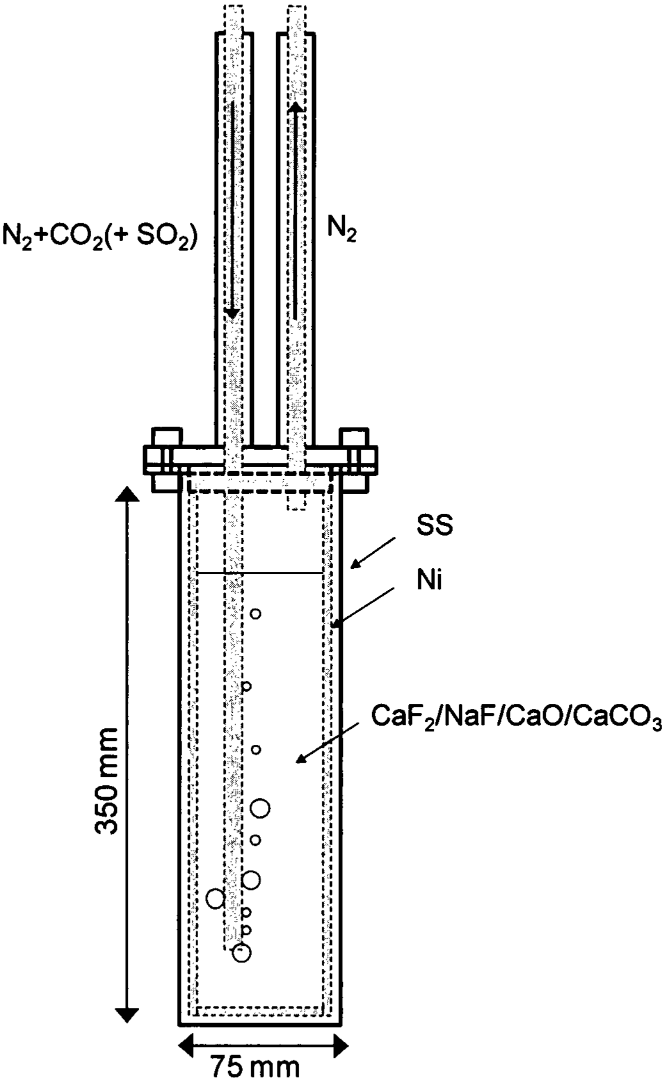

Figure 7

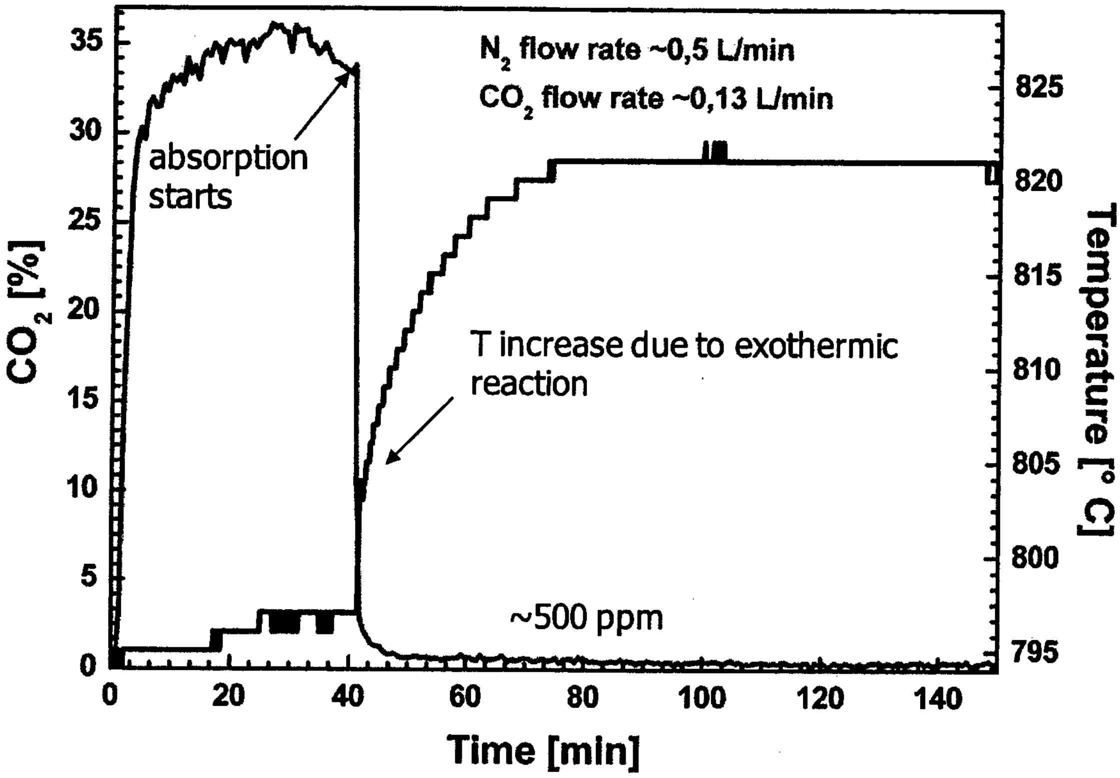

Figure 8

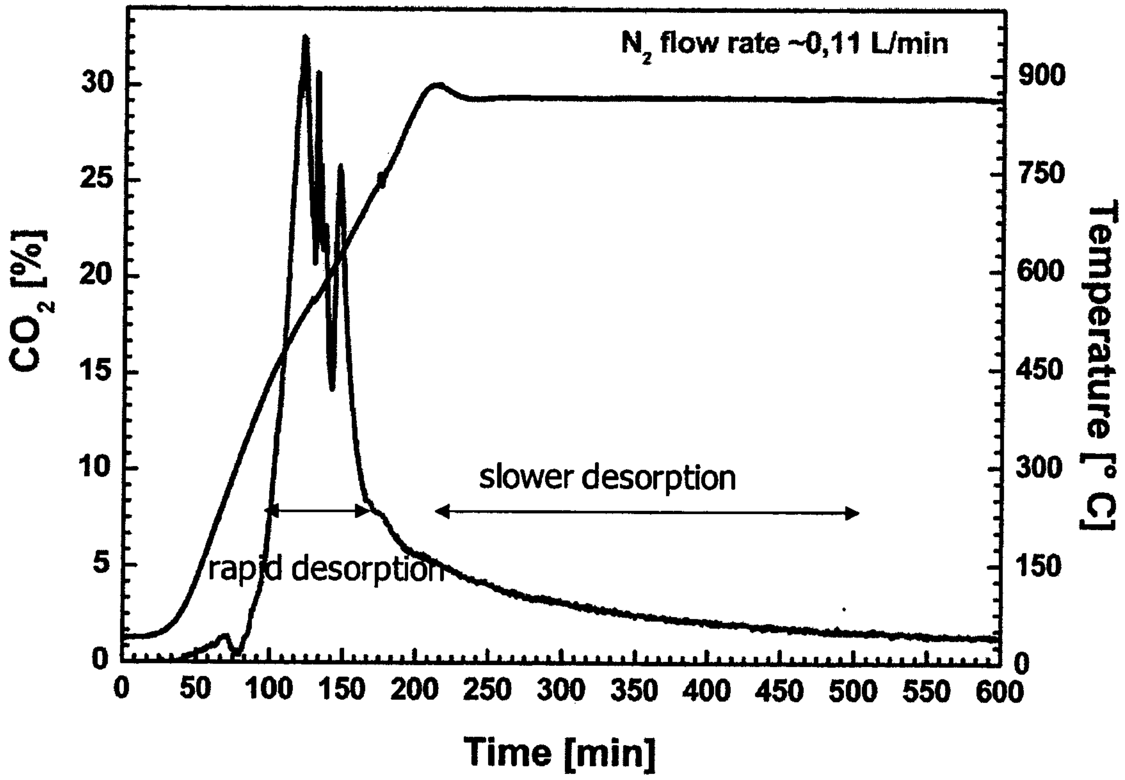

Figure 9

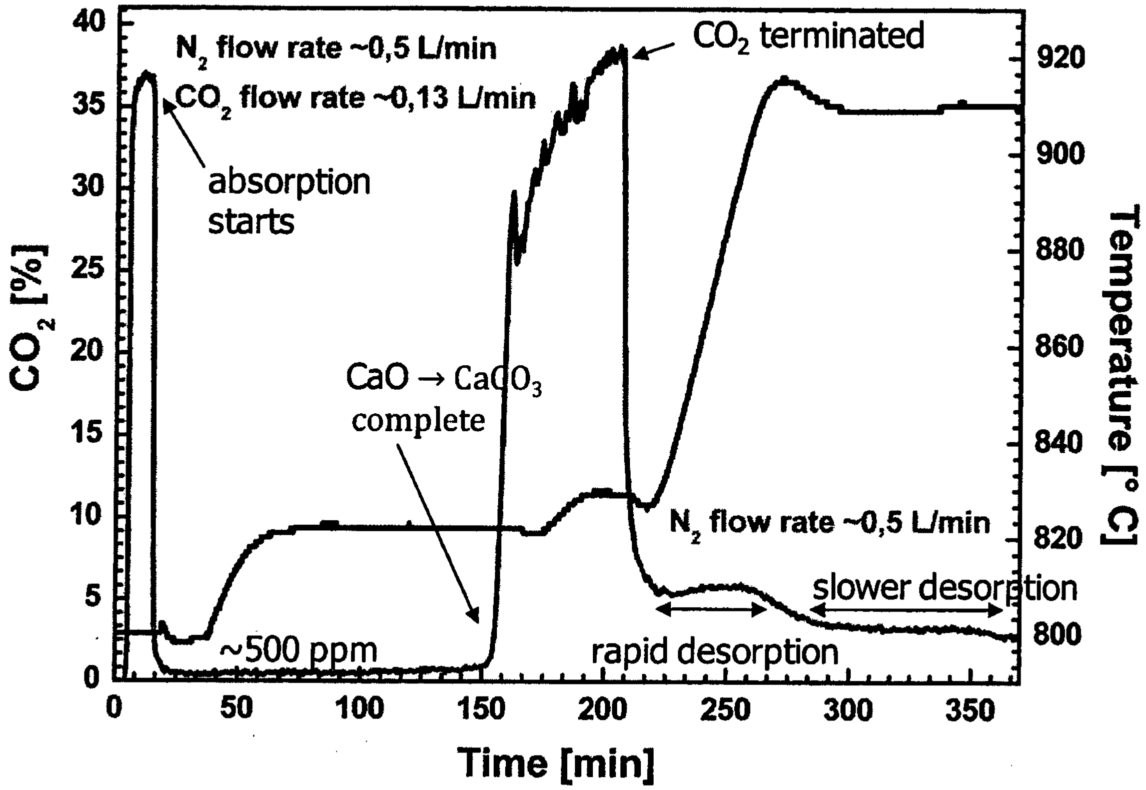
N_2 flow rate ~0,5 L/min
CO_2 flow rate ~0,13 L/min
absorption starts
CO_2 terminated
$CaO \rightarrow CaCO_3$ complete
~500 ppm
N_2 flow rate ~0,5 L/min
rapid desorption
slower desorption
CO_2 [%]
0
5
10
15
20
25
30
35
40
Temperature [° C]
800
820
840
860
880
900
920
Time [min]
0
50
100
150
200
250
300
350

Figure 10

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO2011/000334

A. CLASSIFICATION OF SUBJECT MATTER

B01D 53/14 (2006.01), B01D 53/62 (200601), B01D 53/78(2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(2006.01): B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
SE DK FI NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPODOC, WPI, COMPENDEX, FULLTEXT PATENT, PATGRANSK

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,D	US 2005/0036932 A1 (TAKAHASI TATSUHITO et. al), 2005.02.17, see the whole document	1-8
A,D	RU 2293350 C1 (INSTITUT KATALIZA IM), 2004.05.27, see abstract and drawing	1-8
E	WO 2010/137995 A1 (UNIVERSITETET FOR MILJØ- OG BIOVITENSKAP), 2010.12.02	1-8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search 15/02/2012	Date of mailing of the international search report 16/02/2012
Name and mailing address of the ISA/ Nordic Patent Institute Helgeshøj Allè 81, 2630 Taastrup Facsimile No. +45 43 50 80 08	Authorized officer Iren Beisvåg Telephone No. +47 22 38 74 73

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/NO2011/000334

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2005036932 A1	2005.02.17	WO 0025899 A1	2000.05.11
		CA 2352969 A1	2000.05.11
		JP 2000197810 A	2000.07.18
		EP 1142629 A1	2001.10.10
		CN 1323240 A	2001.11.21
		TW 469165B B	2001.12.21
		US 2001054253 A1	2001.12.27
		CN 1721043 A	2006.01.18
		US 2007154380 A1	2007.07.05
RU 2293350 C2	2007.02.10	None	
WO 2010137995 A1	2010.12.02	NO 330584B B1	2010.11.29
		CA 2763254 A1	2010.12.02