



(86) Date de dépôt PCT/PCT Filing Date: 2010/09/01
(87) Date publication PCT/PCT Publication Date: 2011/03/24
(85) Entrée phase nationale/National Entry: 2012/03/12
(86) N° demande PCT/PCT Application No.: US 2010/047426
(87) N° publication PCT/PCT Publication No.: 2011/034726
(30) Priorités/Priorities: 2009/09/15 (US12/560,004);
2009/11/20 (US12/622,653); 2009/12/16 (US12/639,597)

(51) Cl.Int./Int.Cl. *B01D 53/14* (2006.01),
B01D 53/18 (2006.01), *B01D 53/62* (2006.01)

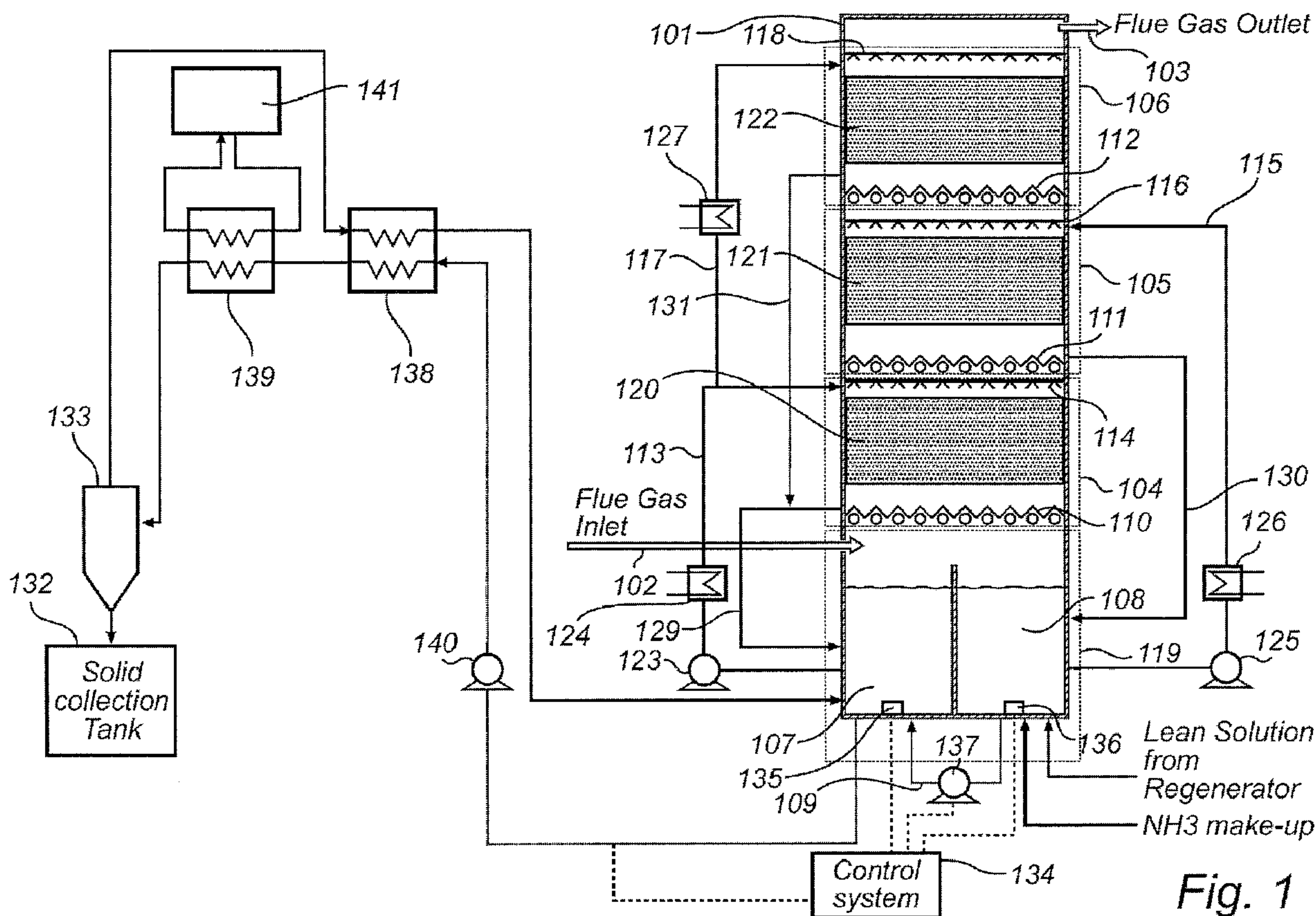
(71) Demandeur/Applicant:
ALSTOM TECHNOLOGY LTD, CH

(72) Inventeurs/Inventors:
KOZAK, FREDERIC ZENON, US;
BLACK, SEAN EDWARD, US;
DUBE, SANJAY KUMAR, US;
MURASKIN, DAVID JAMES, US

(74) Agent: SMART & BIGGAR

(54) Titre : PROCEDE ET SYSTEME D'EXTRACTION DU DIOXYDE CARBONE PRESENT DANS UN GAZ DE
PROCESSUS

(54) Title: METHOD AND SYSTEM FOR REMOVAL OF CARBON DIOXIDE FROM A PROCESS GAS



(57) Abrégé(suite)/Abstract(continued):

the process gas, wherein the molar ratio, R , of ammonia to carbon dioxide in the ammoniated solution is controlled such that substantially no precipitation of solids occurs within the absorption arrangement 101; allowing ammoniated solution including captured carbon dioxide to exit the absorption arrangement 101; cooling the ammoniated solution that has exited the absorption arrangement, wherein at least a part of the captured carbon dioxide is precipitated as solid salt; separating at least a part of the precipitated salt from the ammoniated solution; heating the ammoniated solution from which the at least a part of the precipitated salt has been separated, such that substantially no solids are present in the heated ammoniated solution; and allowing the heated ammoniated solution to re-enter the absorption arrangement 101. Disclosed is also a system for removal of carbon dioxide from a process gas.

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

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
24 March 2011 (24.03.2011)(10) International Publication Number
WO 2011/034726 A1

(51) International Patent Classification:

B01D 53/14 (2006.01) *B01D 53/62* (2006.01)
B01D 53/18 (2006.01)

(72) Inventor; and

(75) Inventor/Applicant (for US only): **KOZAK, Frederic Z.**
[US/US]; 830 Meadowfield Drive, Knoxville, Tennessee
37923 (US).

(21) International Application Number:

PCT/US2010/047426

(74) Agents: **OLSON, Timothy, J.** et al.; ALSTOM Power
Inc., 200 Great Pond Drive, P.O. Box 500, Windsor, CT
06095-0500 (US).

(22) International Filing Date:

1 September 2010 (01.09.2010)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

12/560,004 15 September 2009 (15.09.2009) US
12/622,653 20 November 2009 (20.11.2009) US
12/639,597 16 December 2009 (16.12.2009) US(71) Applicant (for all designated States except US): **AL-
STOM TECHNOLOGY LTD** [CH/CH]; Brown Boveri
Strasse 7, CH-5400 Baden (CH).

(72

WO 2011/034726 A1

Published:

— *with international search report (Art. 21(3))*

METHOD AND SYSTEM FOR REMOVAL OF CARBON DIOXIDE FROM A PROCESS GAS

Cross Reference to Related Applications

This application is a Continuation-In-Part of U.S. Patent Application No. 12/622,653, filed November 20, 2009, and is a Continuation-In-Part of U.S.

5 Patent Application No. 12/560,004, filed September 15, 2009, both of which are incorporated by reference herein in their entirety.

Technical Field

10 The present invention relates to a method for removal of carbon dioxide from a process gas by contacting the process gas with an ammoniated solution.

Background

Most of the energy used in the world today is derived from the combustion of carbon and hydrogen containing fuels such as coal, oil and natural gas, as well
15 as other organic fuels. Such combustion generates flue gases containing high levels of carbon dioxide. Due to concerns about global warming, there is an increasing demand for the reduction of emissions of carbon dioxide to the atmosphere, why methods have been developed to remove the carbon dioxide from flue gases before the gas is released to the atmosphere.

20 WO 2006/022885 (U.S. Patent Application No. 11/632,537, filed January 16, 2007, and which is incorporated by reference herein in its entirety) discloses one such method of removing carbon dioxide from a flue gas, which method includes capturing carbon dioxide from the flue gas in a CO₂ absorber by means of an ammoniated solution or slurry. The CO₂ is absorbed by the ammoniated
25 solution in the absorber at a reduced temperature of between 0°C and 20°C, after which the ammoniated solution is regenerated in a regenerator under elevated pressure and temperature to allow the CO₂ to escape the ammoniated solution as gaseous carbon dioxide of high purity.

Summary

30 An objective of the present invention is to improve the method of carbon dioxide absorption with an ammoniated solution.

This objective, as well as other objectives that will be clear from the following discussion, is according to one aspect achieved by a method of
35 removing carbon dioxide from a process gas, the method comprising: contacting

an ammoniated solution with the process gas in an absorption arrangement, the ammoniated solution capturing at least a part of the carbon dioxide of the process gas, wherein the molar ratio, R , of ammonia to carbon dioxide in the ammoniated solution is controlled such that substantially no precipitation of solids occurs

5 within the absorption arrangement; allowing ammoniated solution including captured carbon dioxide to exit the absorption arrangement; cooling the ammoniated solution that has exited the absorption arrangement, wherein at least a part of the captured carbon dioxide is precipitated as solid salt; separating at least a part of the precipitated salt from the ammoniated solution; heating the
10 ammoniated solution from which the at least a part of the precipitated salt has been separated, such that substantially no solids are present in the heated ammoniated solution; and allowing the heated ammoniated solution to re-enter the absorption arrangement.

The absorption arrangement may comprise one or several absorbers, such
15 as absorption stages. A plurality of absorbers of the absorption arrangement may be arranged together in a common frame or casing, or arranged separate from each other only connected via piping, conduits etc. In its simplest design, the absorption arrangement may comprise only one absorber. This simple design will also simplify the carbon dioxide removal method and will reduce the maintenance
20 costs for the arrangement. The absorber or absorbers may be of any design that allows direct contact between the ammoniated solution and the process gas to take place within the absorber.

By contacting the ammoniated solution with the process gas, carbon dioxide may be removed from the process gas and captured by the ammoniated
25 solution by crossing the formed interface between the process gas and the ammoniated solution.

There is a limit to how much carbon dioxide the ammoniated solution may capture, i.e. when the ammoniated solution reaches saturation. This limit depends on e.g. the pressure and temperature of the solution. By cooling the
30 ammoniated solution, the ability of the solution to dissolve the carbon dioxide is reduced, whereby at least a part of the captured carbon dioxide is precipitated as solid salt. Even if the ammoniated solution has not reached saturation in the absorption arrangement and no solids have been precipitated prior to the cooling of the solution, the cooling of the ammoniated solution may allow for precipitation
35 of captured carbon dioxide in the form of a solid salt. Thus, at least part of the captured carbon dioxide may be separated from the ammoniated solution, e.g. by a separator, by removing at least a part of the precipitated solids.

The ammoniated solution after separation may be saturated with carbon dioxide since only the carbon dioxide in solid precipitated form is removed, not carbon dioxide dissolved in the solution. By heating the ammoniated solution, the ability of the solution to dissolve carbon dioxide is increased even though the molar ratio R is unchanged, allowing the ammoniated solution to return to the absorption arrangement to capture more carbon dioxide without precipitation of solids.

By cooling the ammoniated solution, removing the solids, and re-heating the solution, most of the ammoniated solution may be returned to the absorption arrangement to capture more carbon dioxide without precipitation of solids. Thus, there is no need to regenerate the entire solution stream. Instead, the much smaller volume of solids, and optionally some solution, removed by separation and having a much higher carbon dioxide concentration may be transferred to a regenerator. Since the regenerator applies increased pressure and temperature to the solid material, solution, suspension or slurry being regenerated in order to obtain leaving carbon dioxide of high purity, the energy consumption is much reduced if the volume of the solution, suspension or slurry is reduced and the carbon dioxide concentration is increased.

Also, by inducing precipitation of solids by cooling the ammoniated solution, carbon dioxide in the form of solid salt may be removed from the ammoniated solution even though the ammoniated solution exiting the absorption arrangement contains no precipitated solids, i.e. the ammoniated solution exiting the absorption arrangement might be rich in carbon dioxide but not completely saturated or supersaturated and still allow for removal of carbon dioxide in solid form by e.g. a separator. This implies that the precipitation of solids within the absorption arrangement and the absorber may be avoided compared with if no cooling was performed.

Precipitation of solids in the absorption arrangement may be undesirable since the solids may clog pipes, valves, pumps, absorbers etc., and may also increase the wear of the absorption arrangement due to increased abrasion by the ammoniated solution flow. If there is no precipitation in the absorption arrangement, the absorption arrangement may not have to be designed to accommodate for solid particles in the ammoniated solution whereby the absorption arrangement may be designed in a simpler and cheaper way and for more efficient carbon dioxide capture, e.g. by a more effective packing material in the absorber if a packing material is used, which packing material might otherwise be clogged and result in excessive pressure drop. Also, the maintenance of the absorption arrangement may be greatly reduced.

78396-183

ammoniated solution composition and flow rate, of each absorption stage to be varied within a wide range.

The system may further comprise a control system configured to maintain the mole ratio R of the ammoniated solution in the first sump vessel within a
5 range of 1.8 to 2.5.

The system may further comprise a control system configured to maintain the mole ratio R of the ammoniated solution in the second sump vessel within a range of 2.0 to 4.5.

The system may further comprise a control system configured to maintain
10 the temperature of the first sump vessel within a range of 10 to 25°C, conveniently within a range of 15-20°C.

The system may further comprise a control system configured to maintain the temperature of the second sump vessel within a range of 10 to 25°C, conveniently within a range of 15-20°C.

15 The system may comprise a single control system configured to maintain the temperature and/or R value of the first and/or the second sump vessels, or the system may comprise separate control systems for maintaining temperatures and R values, or for maintaining the first and the second sump vessels.

In an embodiment, the control system comprises a device configured to
20 introduce NH_3 or a medium having an R higher than the R of the ammoniated solution in at least one of the sump vessels into the ammoniated solution of that sump vessel.

The above described and other features are exemplified by the following figures and detailed description.

25

Brief Description of the Drawing

Referring now to the figure, which is an exemplary embodiment:

Fig. 1 is a diagram generally depicting an embodiment of a CO_2 capture system that includes a multi-stage absorbing arrangement with two sump
30 vessels.

78396-183

heat exchanger (124), the first heat exchanger (124) and the separator (133), the separator (133) and the second heat exchanger (138), as well as the second heat exchanger (138) and the absorption arrangement (101).

5 The process gas may be any type of process gas containing carbon dioxide, such as process gas from any combustion device such as furnaces, process heaters, incinerators, package boilers, and power plant boilers.

The ammoniated solution may be any type of solution containing ammonia, such as a liquid solution, especially an aqueous solution. The

