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(54) Title: SCRUBBING OF AMMONIA WITH UREA AMMONIUM NITRATE SOLUTION

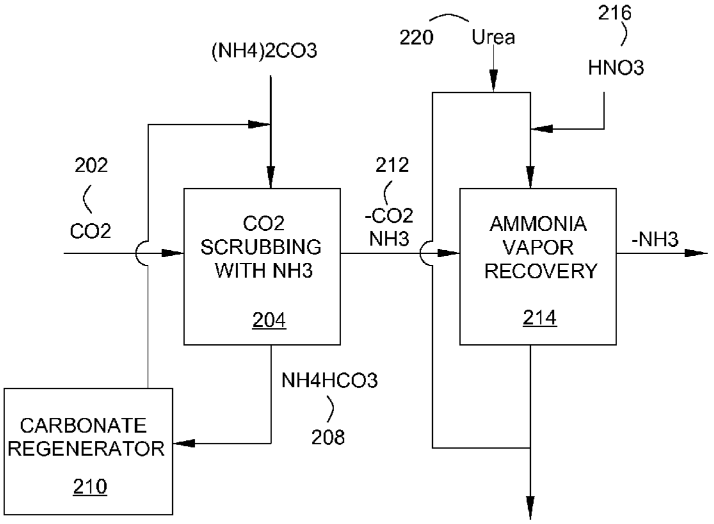

Fig. 2

(57) Abstract: A process for scrubbing ammonia in a C02 removal process having the steps of absorbing (204) at least some CO2 from a gas stream (202) with an ammonium carbonate solution or a mixed alkali solution, resulting in a release of > ammonia; regenerating (210) ammonium.carbonate or mixed alkali solution to produce a concentrated C02 stream; capturing ammonia with an ammonia capture mass transfer apparatus (214). with a concentrated urea ammonium nitrate solution; adjusting the pH of the urea ammonium nitrate soution to between 4 • and 6 with nitric acid; and adding urea to the urea ammonium nitrate solution, thereby producing a urea ammonium nitrate (UAN) fertilizer product ready for cemmercial distribution.

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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

SCRUBBING OF AMMONIA WITH UREA AMMONIUM NITRATE SOLUTION

BACKGROUND

1. Field of the Invention.

The invention is in the field of absorbing ammonia in flue gas scrubbing.

2. Description of the Related Art.

Scrubbing of carbon dioxide with ammonium carbonate solutions has been known for many years. One process for absorbing CO_2 uses either an ammonium carbonate solution or a mixed alkali solution, which can be ammonium and either potassium or sodium carbonate. However, due to the volatility of ammonia at the pHs required for carbon dioxide capture, it is necessary to capture any ammonia released from the solution if the process is to be used to remove CO_2 from flue gas. What is needed, therefore, is a method and apparatus for scrubbing ammonia vapor in a CO_2 scrubbing system.

SUMMARY

The invention is a method and apparatus that satisfies the need for scrubbing ammonia vapor in a CO_2 scrubbing system. One method of absorbing the ammonia vapor is to use a urea solution that is pH adjusted with nitric acid to form a urea ammonium nitrate solution (UAN). Urea ammonium nitrate is composed of 30 – 35 wt% urea, 40 – 45 wt% ammonium nitrate, and 20 – 30 % water and is a fertilizer that contains 28 – 32% nitrogen. The specific gravity of the solution ranges from 1.283 to 1.320 and has a pH of 7 – 7.5. When nitric acid and urea are combined in a ratio that produces a solution that is ammonia lean, the solution will have a pH of 4 – 6 and can be used with an appropriate mass transfer device to absorb ammonia. These and other features, aspects, and advantages of the present invention will become better understood with regard to the following description, claims, and accompanying drawings.

DRAWINGS

Fig. 1 is a process flow diagram showing some of the components used to carry out the process of the present invention.

Fig. 2 is a process flow diagram describing the process of the present invention.

DESCRIPTION

The invention is a method and apparatus that satisfies the need for scrubbing ammonia vapor in a CO_2 scrubbing system. As shown in Fig. 1, the ammonium carbonate or mixed alkali solution 102 is circulated to absorb CO_2 from a flue gas stream containing CO_2, H_2O, O_2, and N_2 104. The solution is sent through a regenerator 106 to produce a concentrated CO_2 stream 108 ready for sequestration. Once regenerated the solution is recycled back to the CO_2 capture section 110 to absorb more CO_2. In the process of absorbing CO_2 ammonia is released. The amount of ammonia released is determined by the conditions of absorption and the composition of the absorbing solution but will be between 100 – 8000 ppm. After the CO_2 is captured, the flue gas moves to an ammonia capture mass transfer section 112 where a concentrated urea ammonium nitrate solution is circulating. The solution is pH adjusted to between 4 and 6 with nitric acid 114 to make the solution ammonia lean and forms ammonium nitrate as shown in equation (1).

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \qquad (1)$$

Urea 116 is added to the solution either prior to the NH_3 capture 112 or after the formation of the ammonium nitrate to maintain a concentrated urea ammonium nitrate solution 118 ready for commercial distribution.

As shown in Fig. 2, a flue gas stream containing CO_2 202 is brought into an absorption section 204 that uses an ammonium carbonate solution to absorb CO_2. The ammonium carbonate is converted into ammonium bicarbonate 208 through reaction of CO_2 with CO_3^{2-} as shown in (2):

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2\ HCO_3^{-} \qquad (2)$$

The ammonium bicarbonate solution is introduced into the regenerator 210, to reverse reaction (2) creating a concentrated CO_2 stream, which can be processed for sequestration or beneficial use. The regenerated solution is re-introduced into the absorber tower 204 to remove more CO_2.

Due to the volatility of the ammonium carbonate solution, the flue gas exits the absorber 204 with >70% CO_2 having been removed and with the addition of ammonia vapor. The CO_2 lean flue gas 212 now enters an ammonia vapor recovery 214 section to remove the ammonia vapor prior to leaving the stack. In the ammonia vapor recovery section, nitric acid 216 is added to a urea ammonium nitrate (UAN) solution to decrease the pH to <6. The UAN absorbs the ammonia vapor from the flue gas in a gas liquid contactor. When the UAN exits the contactor, part of the solution is removed as product 218 ready to be used as a fertilizer product while the rest is recycled back to the ammonia vapor recovery section 214. Additional urea 220 and HNO_3 acid 216 are added to maintain the required ratios of UAN and to maintain the ability to absorb NH_3 vapor.

The advantages of using UAN to do ammonia absorption as part of a CO_2 scrubbing process are:

1. The ability to produce a nitrogen fertilizer, which is the predominant plant nutrient required by crops.
2. The ability to produce a nitrogen fertilizer with minimal capital cost. Since the ammonia capture is required in the CO_2 scrubbing process, only incremental increases are required for the nitrogen fertilizer production including pumps and storage allowing one to take advantage of the infrastructure already in place.

Although the preferred embodiments of the present invention have been described herein, the above description is merely illustrative. Further modification of the invention herein disclosed will occur to those skilled in the respective arts and all such modifications are deemed to be within the scope of the invention as defined by the appended claims.

CLAIMS

What is claimed is:

1. A process for absorbing ammonia in a CO_2 removal process comprising the steps of:

absorbing at least some CO_2 from a gas stream with an ammonium carbonate solution or a mixed alkali solution, thereby releasing ammonia; and

absorbing ammonia using an ammonia absorption process, the ammonia absorption process comprising the steps of:

providing a urea ammonium nitrate solution;

adding an amount of nitric acid to the urea ammonium nitrate solution thereby making the solution ammonia lean; and

contacting the ammonia with the ammonia lean solution to absorb ammonia and make an ammonium nitrate rich solution.

2. The process of claim 1, wherein the amount of nitric acid added is effective to change the pH to between 4 and 6.

3. The process of claim 1, further comprising the step of withdrawing ammonium nitrate.

4. The process of claim 3, further comprising the step of adding urea to the urea ammonium nitrate solution before contacting with ammonia.

5. The process of claim 3, further comprising the step of adding urea to the urea ammonium nitrate solution after contacting with ammonia.

6. A process for absorbing ammonia in a CO_2 removal process comprising the steps of:

absorbing at least some CO_2 from a gas stream with an ammonium carbonate solution or a mixed alkali solution, thereby releasing ammonia; and

absorbing ammonia using an ammonia absorption process, the ammonia absorption process comprising the steps of:

providing a urea ammonium nitrate solution;

adjusting the pH of the urea ammonium nitrate solution to between 4 and 6, and thereby making the solution ammonia lean; and

contacting the ammonia with the ammonia lean solution to absorb ammonia and make an ammonium nitrate rich solution.

7. The process of claim 6, wherein adjusting the pH to between 4 and 6 is done by adding an effective amount of nitric acid.

8. The process of claim 6, further comprising the step of withdrawing ammonium nitrate.

9. The process of claim 8, further comprising the step of adding urea to the urea ammonium nitrate solution before contacting with ammonia.

10. The process of claim 8, further comprising the step of adding urea to the urea ammonium nitrate solution after contacting with ammonia.

11. A process for absorbing ammonia from a gas stream comprising the steps of:

providing a urea ammonium nitrate solution;

adding an amount of nitric acid to the urea ammonium nitrate solution thereby making the solution ammonia lean; and

contacting the ammonia with the ammonia lean solution to absorb ammonia and make an ammonium nitrate rich solution.

12. The process of claim 11, wherein the amount of nitric acid added is effective to change the pH to between 4 and 6.

13. The process of claim 11, further comprising the step of withdrawing ammonium nitrate.

14. The process of claim 13, further comprising the step of adding urea to the urea ammonium nitrate solution before contacting with ammonia.

15. The process of claim 13, further comprising the step of adding urea to the urea ammonium nitrate solution after contacting with ammonia.

16. A process for absorbing ammonia from a gas stream comprising the steps of:

providing a urea ammonium nitrate solution;

adjusting the pH of the urea ammonium nitrate solution to between 4 and 6, and thereby making the solution ammonia lean; and

contacting the ammonia with the ammonia lean solution to absorb ammonia and make an ammonium nitrate rich solution.

17. The process of claim 16, wherein adjusting the pH to between 4 and 6 is done by adding an effective amount of nitric acid.

18. The process of claim 16, further comprising the step of withdrawing ammonium nitrate.

19. The process of claim 18, further comprising the step of adding urea to the urea ammonium nitrate solution before contacting with ammonia.

20. The process of claim 18, further comprising the step of adding urea to the urea ammonium nitrate solution after contacting with ammonia.

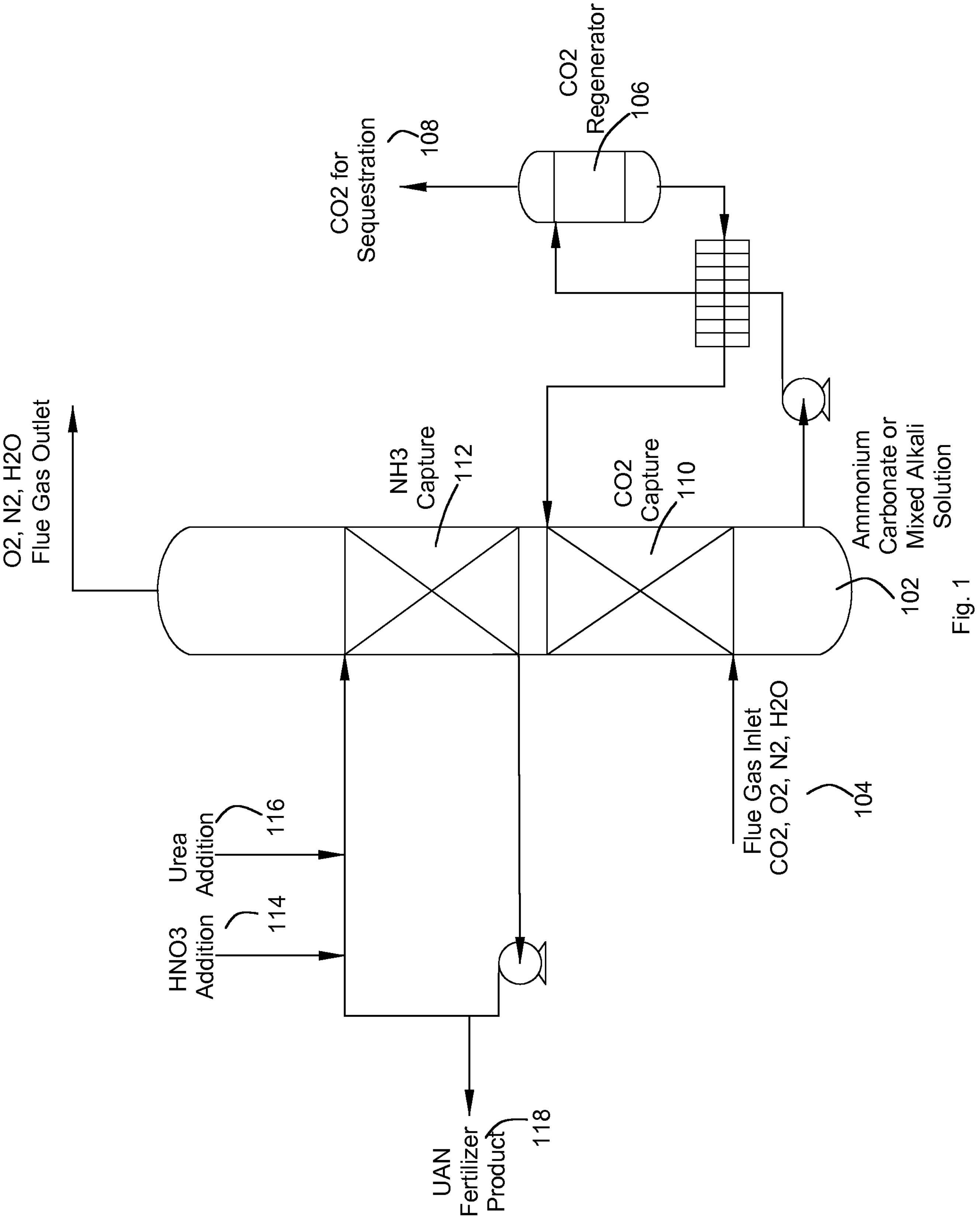
CO2 for Sequestration
108
CO2 Regenerator
106
O2, N2, H2O Flue Gas Outlet
NH3 Capture
112
CO2 Capture
110
Ammonium Carbonate or Mixed Alkali Solution
102
HNO3 Addition
114
Urea Addition
116
Flue Gas Inlet CO2, O2, N2, H2O
104
UAN Fertilizer Product
118

Fig. 1

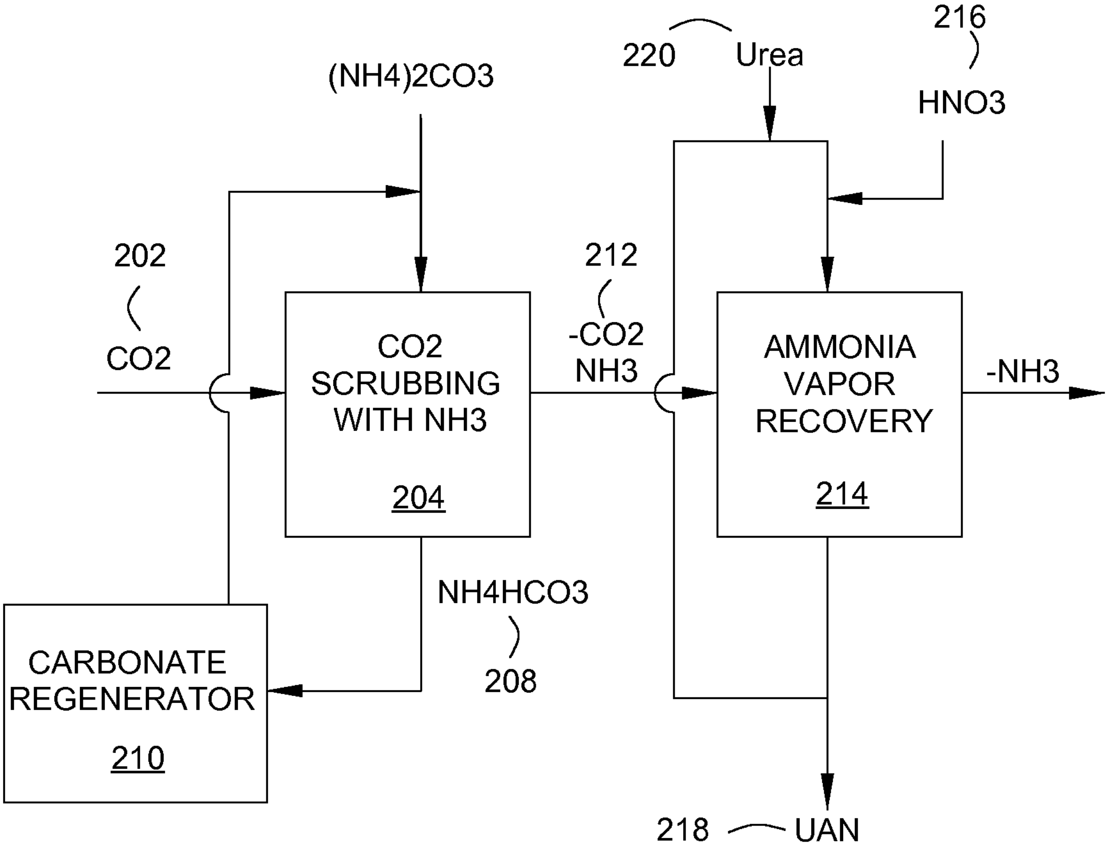
(NH4)2CO3
220
Urea
216
HNO3
202
CO2
CO2 SCRUBBING WITH NH3
204
212
-CO2
NH3
AMMONIA VAPOR RECOVERY
214
-NH3
NH4HCO3
208
CARBONATE REGENERATOR
210
218
UAN

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2008/069771

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/14 B01D53/58

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)
B01D C05C C01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 2006/022885 A (GAL ELI [US]) 2 March 2006 (2006-03-02) page 8, lines 8,9; figure 3 page 13, lines 11-13,21,22	1-10
X	EP 0 514 902 A (ENICHEM AGRICOLTURA SPA [IT]) 25 November 1992 (1992-11-25)	11-20
Y	claim 1; figures 2,4; examples 2,3,5; tables 1,2	1-10
X	EP 0 604 720 A (SCHOTT GLASWERKE [DE]; BROEGBERN FLEISCHMEHLFAB GMBH [DE]; ZEISS STIFT) 6 July 1994 (1994-07-06) column 2, line 42 - column 4, line 27; claims 1,6,11; figure	11-20

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☒ 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

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"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

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"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

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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A	US 3 985 523 A (KAUPAS PHILIP F ET AL) 12 October 1976 (1976-10-12) columns 11-12; figures 1,4; table	1-20
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
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