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(54) **Title**: METHOD FOR NEUTRALISATION OF CARBON DIOXIDE EMISSIONS

(57) **Abstract**: The method for neutralisation of carbon dioxide emissions consists in passing carbon dioxide-containing industrial gases or carbon dioxide isolated from industrial gases through an aqueous solution of a sodium salt of carbonic acid or a sodium salt of a strong inorganic acid, preferably through a sodium chloride solution or a sodium sulfate(VI) solution, with an amount of ammonia stoichiometric in relation to the acidic anion being added. The reaction is carried out at a temperature not exceeding 60°C. The precipitated sodium bicarbonate is isolated from the aqueous solution, washed with methanol, dried in a carbon dioxide atmosphere and stored.

Method for neutralisation of carbon dioxide emissions

The invention relates to a method for neutralisation of carbon dioxide emissions by enabling its long-term storage.

The issue of carbon dioxide emissions, particularly from industrial processes, is an important ecological problem. Carbon dioxide, already present in the surrounding air, is practically impossible to be captured and removed. Therefore, it is necessary to focus on industrial processes, in which the carbon dioxide emitted into the atmosphere is formed on a large scale.

Several methods for CO_2 capture from waste gases are known. The issue has long been dealt with; however, the majority of known methods is based on fixation of carbon dioxide in solutions of sodium or potassium carbonate, or by sodium carbonate in the solid form. The resulting sodium bicarbonate is washed with water on sieves, and the captured carbon dioxide is then liberated in a controlled manner and directed to industrial processes. The sodium carbonate solution or solid sodium carbonate is recycled to another process of carbon dioxide fixation. Usually, the amounts of captured carbon dioxide exceed the demand for this raw material. This raises the further issue of how to store the excess CO_2.

Draft amendments to legislation that would allow for underground storage of carbon dioxide on an industrial scale in Poland raises concern and causes some scientists to warn of the injection of CO_2 into the ground. Carbon dioxide of industrial origin is to be injected to a depth of 1390-1550 metres. Exhausted natural gas deposits, as well as coal deposits (unexhausted) with methane, are the best locations for CO_2 storage. However, it is the saline layers of underground waters which are the most prospective. Some pilot projects are under way, consisting in injecting CO_2 into deep saline aquifers. Pilot projects connected with CO_2 capture and storage are implemented in many countries. In order for this storage type to be safe, constant monitoring of underground carbon dioxide deposits is necessary, as it is a gas posing a risk of explosion. Underground storage of carbon dioxide raises numerous controversies, and many scientists are warning against it. CO_2 injected under the ground migrates in various directions in an uncontrolled manner. If it penetrates water resources, it will acidify them, as CO_2 forms carbonic acid with water. Additionally, there is a risk of the CO_2 exploding, as in Cameroon, where carbon dioxide accumulated spontaneously. The scientific community believes that the no-

tank storage of liquefied CO_2 in geological deposits is highly risky and dangerous for the environment, and it may lead to effects on a global scale that cannot be foreseen at present. Moreover, the so-accumulated CO_2 reserves cannot be used as a raw material for other chemical processes in the future, e.g. in the Solvay process.

Alternatively, carbon dioxide liquefied under pressure may be stored in metal tanks. These tanks, being pressure tanks, must be made of steel of a proper quality, and they must exhibit chemical and mechanical resistance. One should also note that over time, the tanks will undergo corrosion, and they will pose a hazard to the environment through violent emission of large amounts of carbon dioxide. The volume that would be occupied by such tanks forces the finding of vast disposal grounds for them.

The invention relates to a method for neutralisation of carbon dioxide emissions by its storage in the form of a solid chemical compound, resistant to spontaneous decomposition.

According to the invention, carbon dioxide-containing industrial gases or carbon dioxide isolated from industrial gases are passed through an aqueous solution of a sodium salt of carbonic acid or a sodium salt of a strong inorganic acid, preferably through a sodium chloride solution or a sodium sulfatedm(VI) solution, with an amount of ammonia stoichiometric in relation to the acidic anion being added. The reaction is carried out at a temperature not exceeding 60°C. The precipitated sodium bicarbonate is isolated from the aqueous solution, washed with methanol, dried in a carbon dioxide atmosphere and stored.

The reaction of carbon dioxide leading to sodium bicarbonate being a solid consists in permanent bonding of carbon dioxide gas with the formation of a sodium salt. This substance is stable up to 75°C and is safe to use. Moreover, it is not toxic and is sometimes used in the household. Sodium bicarbonate is manufactured on a small scale from specially purified sodium carbonate (Na_2CO_3). Sodium carbonate is less preferable as a CO_2-storing salt, because of the fact that it already contains more than 41.5% of CO_2. Sodium bicarbonate contains almost 52.4% of CO_2, so it is more effective as a carbon dioxide "tank".

As a result, the carbon dioxide is transformed into an easily storable and stable solid, which does not require additional supervision costs or construction of specialist warehouses.

At the storage stage, of key importance are retention and safe and prolonged storage of the maximum amount of the isolated carbon dioxide. In Poland, the best approach is to use commonly available sodium chloride NaCl, generating ammonium chloride, or also the rather inexpensive and easily available sodium sulfate(VI), generating ammonium sulfate(VI) used in agriculture. In both of these methods, ammonia is used, manufactured mostly for agriculture as a component of nitrogen fertilisers directly or in the form of a salt. As mentioned above, in the case of CO_2 "storage", it is important that the carbon dioxide which has already been stored is not lost. Therefore, two conditions must be met: the process of generation of the storing substance must be inexpensive and highly efficient, and it must not be conducive to a loss of CO_2 after storage. There is also a third condition: to avoid generation of more waste than was stored during the process. It has been found that washing of sodium bicarbonate with methanol, applied according to the invention, and carrying out the drying in a carbon dioxide atmosphere promotes a greater stability of sodium bicarbonate than in case when washing is carried out conventionally with water, as in known processes of sodium bicarbonate preparation.

It is generally acknowledged that to a temperature up to 70°C, sodium bicarbonate is an absolutely stable substance, but weak absorption of heat from heating elements by flaking crystals may cause local overheating of heating elements and the exceeding of this temperature. Therefore, the removal of methanol was carried out in a carbon dioxide atmosphere, which facilitates methanol removal by decreasing the concentration of methanol vapours in the gaseous phase, simultaneously hindering the $NaHCO_3$ decomposition process. The latter leads to stalling the process of loss of CO_2 already stored in the crystals.

The following examples illustrate the method according to the invention more closely, without limiting its scope.

Example 1

The following apparatus was used for the synthesis: a three-necked, round-bottomed flask with a capacity of 2 dm^3, placed in a water bath, equipped with a stirrer; a tube supplying carbon dioxide through a washer and reaching almost to the bottom of the flask, but next to the stirrer, and a thermometer. There is a gas outlet with a washer next to the stirrer's gland. For regeneration of methanol, a separate apparatus was used, consisting of a three-necked, round-bottomed flask with a capacity of 2 litres,

equipped with a dephlegmator terminated with an adapter with a thermometer, discharging vapours to a condenser. Carbon dioxide was also supplied for regeneration of methanol through a washer. The flask was placed in a glycerol bath with a maintained temperature not higher than 125°C. The filtering assembly, or the Büchner funnel, was equipped with a filter paper. A round-bottomed flask for removal of methanol from the precipitate, also with a capacity of 2 litres, was placed in a water bath with a maintained temperature below 80°C. This flask was equipped with a manual stirrer, carbon dioxide supply and vapour outlet to a condenser. 8300 g of a solution containing 790.45 g of ammonia and 7509.55 g of water were prepared. Separately, 8 portions of NaCl salt 339.02 g each were prepared, as well as a cylinder with liquefied carbon dioxide equipped with a reducing valve.

Execution

1037.5 g of the ammonia solution and one 339.02 g portion of NaCl were placed in the synthesis flask. The carbon dioxide supply was started, then the stirrer was turned on and water circulation in the water bath was started while maintaining a temperature below 30°C. After one hour, the temperature in the flask exhibited a distinct downward trend; therefore, after a further 30 minutes, ice was added to the water bath cooling the flask, to observe a temperature decrease to 20°C in the flask after another 30 minutes. The apparatus was disassembled, its content filtered, and then the funnel with the isolated sodium bicarbonate was transferred onto a round-bottomed flask, and the precipitate contained in the funnel was washed with a 129.1 g portion of methanol. Next, the precipitate from the Büchner funnel was transferred into the flask for methanol removal. The sets for methanol regeneration and methanol removal were connected and bath heating was turned on. The carbon dioxide supply to the flask for methanol removal was then started, and the stirrer was operated manually. After 2.5 hours, the process of methanol regeneration and methanol removal from the precipitate was completed, recovering 127.1 g of methanol in total. Then, $NaHCO_3$ synthesis was repeated six more times in the manner described above, using the same amounts of substances but swapping the synthesis flask with the flask for methanol regeneration each time without cleaning. The following portions of dry precipitate were obtained in these tests:

Portion 1	415.3 g
Portion 2	418.8 g
Portions 3, 4, 5, 6, 7	419.0 g each

After combining portions 3, 4, 5, 6 and 7, 2095.0 g of $NaHCO_3$ were obtained in total, using 1695.1 g of NaCl in total.

Example 2

The same apparatus and procedure as in Example 1 were used.

6484.0 g of a solution containing 790.45 g of ammonia and 5693.55 g of water was prepared for the test.

Separately, eight portions of anhydrous sodium sulfate(VI) Na_2SO_4 in an amount of 412.0 g each were prepared, as well as a cylinder with liquefied carbon dioxide equipped with a reducing valve.

Execution

810.5 g of the ammonia solution was poured into the synthesis flask, and the carbon dioxide supply was started. The stirrer was then turned on, and water circulation in the water bath was started, while maintaining the temperature in the flask below 27°C. During the stirring and cooling, a portion of 412.0 g of sodium sulfate(VI) was introduced. The process was continued whilst trying to maintain the temperature in the flask below 30°C, until a downward trend of the temperature was observed. The subsequent procedure was the same as in Example 1, but 136 g of methanol was used for washing the sodium bicarbonate precipitate each time. After the completion of the 7th portion, the process was balanced as in Example 1, and similarly, portions 3, 4, 5, 6 and 7 were combined, obtaining 2192.4 g of $NaHCO_3$ in total, while using 2060.0 g Na_2SO_4 in total, or an amount corresponding to 1695.1 g NaCl.

Example 3

For storing the same amount of carbon dioxide as in Examples 1 and 2, sodium carbonate Na_2CO_3 was used as a raw material, produced in industry in very large amounts. The process was carried out using the same procedure and apparatus as in Example 1.

12 portions of sodium carbonate 384.31 g each and 1580 g of water in total, as well as a carbon dioxide cylinder equipped with a reducing valve, were prepared. Separately, one portion of an aqueous solution saturated with sodium bicarbonate in an amount of 751.9 g at 20°C was also prepared in the synthesis flask.

Execution

131.63 g of water and one 384.31 g portion of sodium carbonate were introduced into the synthesis flask containing the saturated aqueous solution of sodium bicarbonate. The stirrer and water circulation in the cooling bath were started, then the saturation with carbon dioxide was started. When a temperature decrease in the flask was observed, cooling was intensified by adding a small amount of ice to the water bath, and when the flask reached 20°C, a 20-minute wait was applied. The content was filtered and the procedure was continued as previously, but the precipitate was not washed at all, and it was transferred into the flask for methanol removal and dried in a carbon dioxide stream. The process was repeated nine times more, obtaining:

Portion 1	609.20 g of precipitate
Portions 2, 3, 4, 5, 6, 7, 8, 9 and 10	609.15 g each.

8 portions were used for the balancing, which was the amount corresponding to the same amount of carbon dioxide as in Examples 1 and 2, obtaining 4873.20 g of precipitate in total.

As may be seen, much more sodium carbonate had to be used for storing the same amount of carbon dioxide, storing it in an amount of sodium bicarbonate, which is by almost 2.5 times larger. Therefore, sodium carbonate is a useful raw material in the method according to the invention; however, this requires a larger area for storage.

Claims

1. A method for neutralisation of carbon dioxide emissions by its storage, characterised in that carbon dioxide-containing industrial gases or carbon dioxide isolated from industrial gases are passed through an aqueous solution of a sodium salt of carbonic acid or of a sodium salt of a strong inorganic acid, with an amount of ammonia stoichiometric in relation to the acidic anion being added, and the reaction is carried out at a temperature not exceeding 60°C, and the precipitated sodium bicarbonate is isolated from the aqueous solution, washed with methanol, dried in a carbon dioxide atmosphere and stored.
2. A method according to claim 1, characterised in that sodium chloride or sodium sulfate(VI) is used as the sodium salt of a strong inorganic acid.

INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/62 B01D53/78
ADD.

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 C02F

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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 830 422 A (KRESNYAK STEVE [CA] ET AL) 3 November 1998 (1998-11-03) column 4, line 12 - column 6, line 31; figures 1-3 -----	1,2
A	Michael Kanellos: "Can baking soda curb global warming?", CNET, 27 November 2007 (2007-11-27), pages 1-2, XP055313497, Retrieved from the Internet: URL:https://www.cnet.com/news/can-baking-soda-curb-global-warming/ [retrieved on 2016-10-24] the whole document -----	1
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2008/110405 A2 (SILICON FIRE AG [CH]; KRASS FLORIAN [CH]; GRAUER PETER [CH]) 18 September 2008 (2008-09-18) page 1 - page 3; figure 7	1
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INTERNATIONAL SEARCH REPORT

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