Title: A METHOD AND AN APPARATUS FOR RECOVERING CARBON DIOXIDE FROM FLUE GASES

Abstract: A method and an apparatus for recovering carbon dioxide (CO₂) from flue gases, in which method the flue gases are washed with an alkali metal carbonate containing washing solution in a scrubber (1), which comprises at least one washing stage (A, B, C, D, E). The alkali metal bicarbonate concentration of the solution containing alkali metal bicarbonate, which is formed as a result of washing the flue gases, is increased to such a high level that crystalline alkali metal bicarbonate containing alkali metal bicarbonate slurry is formed.
1

A method and an apparatus for recovering carbon dioxide from flue gases

Field of the invention

5

The invention relates to a method for recovering carbon dioxide from flue gases according to the preamble of the appended claim 1. The invention also relates to an apparatus for implementing the aforementioned method in accordance with the preamble of the appended claim 17.

Background of the invention

The flue gases of a boiler include various gaseous impurities as a result of combustion, such as sulphur and nitrogen oxides and carbon dioxide. The present environmental protection regulations require that flue gases are cleaned and impurities are removed from them prior to releasing flue gases into the environment from a combustion plant. For this purpose, there are several cleaning methods for flue gases that can be selected, for example dry, semidry and wet methods.

In wet cleaning methods flue gases are washed with a solution-like reagent, which reacts with the impurities in the flue gases. The reaction results in compounds, which are not harmful to the environment and which can be removed from the scrubber.

Carbon dioxide is one of the so-called greenhouse gases, which cause climate changes. Most of the carbon dioxide emissions are created in the combustion of fossil fuels. On the other hand, there are several usages of carbon dioxide: it is, for example, used in improving oil recovery from an oil source and in the food industry. Removal and recovery of carbon dioxide from flue gases is therefore not only advantageous for the protection of environment, but also enables the commercial utilization of the recovered carbon dioxide.
Carbon dioxide can be separated from flue gases by washing them with a solution containing a reagent that reacts with carbon dioxide.

These kinds of methods are disclosed, for example, in US patent publications 6,399,030 and US 2004/0253159. In the methods disclosed in these publications amine-based reagents are used as washing solution in different washing stages. A problem with the use of amine-based washing solutions is that the final reaction products going to the waste treatment of the plant are difficult to process. They cannot be taken to the plant’s waste storage area nor to wastewater treatment, because they are harmful substances and they must be carefully prevented from getting into groundwater. Virtually the only disposal way for amine-based reaction products is combustion. In addition, amine-based reagents are expensive. If the flue gases to be cleaned contain a great deal of impurities, the use of amine-based washing solutions is not economical, because cleaning such flue gases uses a great deal of amine reagent.

From US publication 4,510,124 it is known to remove carbon dioxide from sulphur dioxide containing flue gases by washing the flue gases in one stage with a potassium carbonate solution. The used washing solution is regenerated in order to create a usable washing solution, in which regeneration the carbon dioxide separated from the flue gases is used. The problem with this method is expressly the massive washing solution regeneration process it requires. In addition, the carbon dioxide recovered from the flue gases is used entirely in regenerating the washing solution, and none of it can be recovered.

Brief description of the invention

Therefore, the purpose of the present invention is to provide a method for recovering carbon dioxide from flue gases, which avoids the abovementioned problems and with which the carbon dioxide in the flue gases can be commercially utilized. Furthermore, it is an aim of the invention to provide an apparatus implementing the aforementioned method.
To attain this purpose, the method according to the invention is primarily characterized in what will be presented in the characterizing part of the independent claim 1.

The apparatus according to the invention, in turn, is primarily characterized in what will be presented in the characterizing part of the independent claim 17.

The other, dependent claims will present some preferred embodiments of the invention.

The invention is based on the idea that carbon dioxide is separated from flue gases by washing them in a scrubber where a carbonate solution of an alkali metal, such as, for example, sodium carbonate or potassium carbonate solution, is used as washing solution. If sodium carbonate solution is used as washing solution, reaction of the carbon dioxide with the sodium carbonate in the washing solution can be presented according to the following formula:

\[ \text{CO}_2 + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaHCO}_3 \]  \hspace{1cm} (1)

Thus, the reaction result is sodium bicarbonate (NaHCO₃). If the alkali metal carbonate used in the washing solution is potassium carbonate, potassium bicarbonate (KHCO₃) is created in the reaction and the reaction formula is as follows:

\[ \text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{KHCO}_3 \]  \hspace{1cm} (2)

The alkali metal bicarbonate concentration of an alkali metal bicarbonate containing solution is increased by absorbing carbon dioxide into the solution. This can be done, for example, by recycling the solution in scrubber circulation, in which case when the amount of carbon dioxide absorbed into the washing solution increases enough, alkali metal bicarbonate crystals are formed in the solution. The slurry-like
solution containing both crystalline alkali metal bicarbonate and alkali metal bicarbonate solution is led to a separator, where the alkali metal bicarbonate containing solution separated from the slurry is led back to the scrubber and the fraction containing alkali metal bicarbonate crystals is led via a heat exchanger to the stripper. In the stripper the fraction containing alkali metal carbonate crystals is processed by stripping with steam. As a result of the stripping, gaseous carbon dioxide and alkali metal carbonate solution are formed, which alkali metal carbonate solution is directed back to the scrubber. The washing solution used in the scrubber is also produced in the scrubber itself by supplying alkali metal hydroxide solution to it, which solution reacts with the carbon dioxide in the flue gases and forms the alkali metal carbonate solution used as washing solution. The reaction takes place in the following manner, when the solution being added is sodium hydroxide:

$$2\text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$$ \hfill (3)

If the scrubber uses potassium reagents, the added solution is potassium hydroxide with the following reaction:

$$2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$$ \hfill (4)

According to an embodiment of the invention, the scrubber is divided into several washing stages. In the washing stages, alkali metal carbonate solution, alkali metal bicarbonate solution, or a mixture of them is used as washing solution so that the washing stage of the scrubber where the flue gases with the smallest amount of carbon dioxide are washed with a solution, whose alkali metal carbonate concentration is the highest. This washing stage is the stage that is located uppermost in the scrubber in the flow direction of the flue gases. In the washing stages lower in the scrubber the flue gases are washed with washing solutions where the alkali metal carbonate concentration is smaller than in the uppermost stage of the scrubber. In these washing stages the alkali metal bicarbonate concentration increases when going downwards in the scrubber. The alkali metal bicarbonate containing
solution is recycled in the scrubber circulation, in which case alkali metal bicarbonate crystals are formed in it. The slurry-like solution containing alkali metal bicarbonate crystals is led to the separator and from there further to the stripper via a heat exchanger.

According to an embodiment of the invention an additional washing stage is arranged in the scrubber before the washing stages aiming to separate carbon dioxide, in which additional stage the possible sulphur oxides are removed from the flue gases. When sulphur dioxide is removed from the flue gases before the removal of carbon dioxide, the sulphur dioxide does not disturb the recovery of carbon dioxide. Alkali metal carbonate solution is also used in removing sulphur oxides.

An advantage of the invention is that by means of it carbon dioxide can be recovered from the flue gases efficiently and simply. The recovered carbon dioxide can be utilized elsewhere, for example, it can be sold.

In addition, because the fraction taken to the carbon dioxide stripping and containing alkali metal bicarbonate crystals includes as little liquid as possible, i.e. alkali metal bicarbonate solution, the amount of energy required in stripping is smaller. Also, the amount of energy needed for pumping of solutions decreases. In this way, economical savings are provided. With the invention, the liquid/gas ratio required in the absorption of carbon dioxide can be decreased to even half of the process where the aim is not the creation of alkali metal bicarbonate crystals.

An advantage of the invention is also the simplicity of its configuration. The parts of the apparatus required for implementing the invention are all easily commercially available, in which case the invention is easy and fast to implement. The apparatus according to the invention is also easy to install when retrofitting with an already operating scrubber.

In addition, an advantage of the invention is that the washing solution used in recovering carbon dioxide can be produced by regenerating the used washing solution, in which case the amount of make-up chemical
introduced to the process can be kept small. The make-up chemical, alkali metal hydroxide is also a cheap and easily available chemical.

**Brief description of the drawings**

In the following, the invention will be described in more detail with reference to the appended drawings, in which

Fig. 1 shows schematically and in a highly reduced manner an apparatus according to the invention,

Fig. 2 shows schematically and in a highly reduced manner another apparatus according to the invention, and

Fig. 3 shows schematically and in a highly reduced manner the apparatus according to Figure 2, wherein an additional washing stage for removing sulphur oxides is arranged in the scrubber of the apparatus.

In Figures 1, 2 and 3, the same numerals refer to corresponding parts and they will not be explained separately later on, unless required by the illustration of the subject matter.

**Detailed description of the invention**

In this description and in the claims the alkali metal carbonate solution refers to a solution, where the effective reagent is alkali metal carbonate, preferably sodium or potassium carbonate. The solution may also include alkali metal bicarbonate, such as sodium or potassium bicarbonate or other components, which do not, however, substantially take part in the recovery of carbon dioxide according to the invention. The alkali metal bicarbonate solution, in turn, refers to a solution, which includes alkali metal bicarbonate, preferably sodium or potassium bicarbonate, but which may also include alkali metal carbonate and other components. The term line in this description refers to any pipe, duct or channel suitable for conveying a liquid or gaseous matter.
In the example of Figures 1 to 3, which is explained next, sodium reagent, i.e. sodium carbonate and sodium bicarbonate, is disclosed to be used as the alkali metal reagent, but also potassium reagent, i.e. potassium carbonate and potassium bicarbonate, are applicable to be used in the method and they create substantially the same end result. According to the above-presented definitions the sodium carbonate solution may also comprise sodium bicarbonate and correspondingly the sodium bicarbonate solution may comprise sodium carbonate.

Figure 1 is a schematic and a greatly simplified view of an apparatus according to the invention. The apparatus comprises a flue gas scrubber 1 with one washing stage A. The washing stage A includes nozzles 2a distributing washing solution, pipes 3a distributing washing solution and connected to the nozzles, and an tray stage 4a composed of trays 4a'. There are several nozzles 2a and they are arranged at even intervals over the cross-sectional area of the scrubber so that they spray washing solution substantially evenly over the entire cross-sectional area of the scrubber. The tray stage 4a is placed before the nozzles 2a in the flow direction of the flue gases. A droplet separator 5 is placed in the scrubber after the nozzles 2a in the flow direction of the flue gases, which separator separates the droplets that have been swept along with the flue gases. It is also possible to arrange other washing stages in the flue gas scrubber 1, which stages are placed before the tray stage 4a or after the droplet separator in the flow direction of the flue gases. For example, a washing stage E removing sulphur oxides, whose operation is described more in detail in connection with the embodiment of Figure 3, is placed before the tray stage 4a.

The flue gases are supplied to the flue gas scrubber 1 from its lower part, via duct 6. The flow direction of flue gases in the flue gas scrubber is upwards, from the bottom to the top. The flue gases are washed with sodium carbonate solution sprayed via nozzles 2a. Sodium carbonate (Na₂CO₃) reacts with the carbon dioxide in (CO₂) the flue gases and forms sodium bicarbonate solution (NaHCO₃).
Sodium hydroxide solution (NaOH) is also led to the scrubber 1 via line 12 and nozzles 2a to replace the sodium used in washing. Sodium hydroxide solution reacts with the carbon dioxide in the flue gases and forms sodium carbonate solution used as washing solution. The cleaned flue gases are led out via a stack 13 arranged in the upper end of the scrubber.

The sodium bicarbonate containing solution received from the flue gas scrubber 1 is recycled with a pump 8 to a separator 11 via line 7. The solution 11 led to the separator 11, i.e. slurry contains both crystalline sodium bicarbonate and sodium bicarbonate solution, as well as sodium carbonate solution.

The separator 11 processes the sodium bicarbonate slurry and divides it into two fractions. The first fraction contains substantially all the sodium bicarbonate crystals formed in the scrubber, as well as sodium carbonate and sodium bicarbonate solution, and the second fraction comprises sodium carbonate and sodium bicarbonate solution. The separator can be any device suitable for separating different fractions, such as, for example, a gravitation separator based on gravity or a cyclone separator. The second fraction separated in the separator is led via line 9 to the scrubber nozzles 3a. The purpose of recycling is to make the sodium bicarbonate concentration in the solution so high that it crystallizes into the solution, in which case sodium bicarbonate crystals are formed in it.

The first fraction separated in the separator 11 is led with a pump 21 via line 14 to a heat exchanger 15. From the heat exchanger 15 the first fraction is led via line 16 to be processed in a stripper 17. In the heat exchanger 15 the first fraction is heated, which decreases the energy consumption of the stripper.

The purpose of stripping is to by means of heat and pressure form from the first fraction sodium carbonate solution and gaseous carbon dioxide, which sodium carbonate solution is to be used in the scrubber 1. Carbon dioxide is stripped to a gas phase by means of hot steam.
Steam is brought to the stripper via a line 22 connected to its lower part. The carbon dioxide freed in stripping is removed via a line 23 from the upper part of the stripper 17.

The heat exchanger 15 also cools the sodium carbonate solution received from the stripper 17, which cooled solution is led from the heat exchanger 15 via line 18 to act as washing solution in the flue gas scrubber 1. The sodium carbonate solution received from the stripper is led to the heat exchanger 15 via a line 19. A pump 20 arranged in line 19 is utilized in transferring the solution. Cooling the sodium carbonate solution improves the absorption of carbon dioxide into the washing solution.

The heat required by the stripper 17, i.e. the steam used in this embodiment is formed of the sodium carbonate solution received from the stripper 17, which is evaporated in the heat exchanger 35. The sodium carbonate solution is led to the heat exchanger 35 via line 36 with a pump 37 and the steam formed in the heat exchanger is led to the stripper via line 22. The heat needed for evaporating the sodium carbonate solution is brought to the heat exchanger, for example, as steam via line 38. The condensate forming in the heat exchanger 35 is removed via line 39.

Figure 2 shows an embodiment of the invention, where the recovery of carbon dioxide takes place in three stages. To implement this, three washing stages are arranged in the scrubber, a first washing stage B, a second washing stage C and a third washing stage D. The washing stages are arranged consecutively in the scrubber so that the first washing stage B is the lowest in the scrubber, i.e. first in the flow direction of the flue gases, the second washing stage C is after that and the third washing stage D is uppermost in the scrubber.

The washing stages include nozzles 2b, 2c and 2d distributing washing solution, as well as pipes 3b, 3c and 3d distributing washing solution and connected to the nozzles. There are several nozzles 2b, 2c and 2d in each washing stage and they are arranged at even intervals over
the cross-sectional area of the scrubber so that they spray washing solution substantially evenly over the entire cross-sectional area of the scrubber. The flow direction of flue gases in the flue gas scrubber is upwards, from the bottom to the top. The second and third washing stage C and D in addition include packed beds 4c and 4d, which are placed before the nozzles in the flow direction of the flue gases. In the first washing stage B the washing solution sprayed via the nozzles 2b flows in a tray stage 4b composed of trays 4b', in counterflow in relation to the flue gases. After the second washing stage C and the third washing stage D there are droplet separators 5 in the flue gas scrubber, separators which separate the droplets that have been swept along with the flue gases.

The flue gases are supplied to the flue gas scrubber 1 from its lower part, via duct 6. The duct 6 is placed before the first washing stage B so that the flue gases discharged from the duct 6 to the flue gas scrubber 1 are washed first in the first washing stage B of the scrubber, next in the second washing stage C and last in the third washing stage D. The washing solution sprayed to all washing stages flows downwards in the scrubber and it is not removed from there until via a line 7 placed in its lower part. In other words, for example the washing solution sprayed to the third washing stage D via nozzles 2d flows through both the second and the third washing stage.

The washing solution sprayed to the flue gases in each stage contains at least sodium carbonate. Depending on the washing stage it may also contain sodium bicarbonate. In the third washing stage D the washing solution sprayed via the nozzles 2d is almost solely sodium carbonate solution. In the second washing stage C the washing solution sprayed to the flue gases contains both sodium carbonate and sodium bicarbonate, which both substances are in solution form. The washing solution used in the first washing stage B contains sodium carbonate and sodium bicarbonate in solution form, as well as crystalline sodium bicarbonate. By dividing the scrubber into several washing stages and by using washing solutions with different composition in them, the recovery of carbon dioxide can be boosted. The pur-
pose is to make the concentration of the sodium bicarbonate created in the recovery so high that it crystallizes in the solution. Crystallization takes place in the washing stage placed the lowest in the scrubber, i.e. in the first washing stage B. Crystallization takes place according to a principle well known by a person skilled in the art, in which principle the concentration of the substance in the mixture is increased so that the mixture becomes saturated with the substance in question, after which the substance crystallizes. The aim of the second and third washing stages that are uppermost in the scrubber, is to absorb as much of the carbon dioxide contained in the flue gases as possible into the washing solution. Because of this, washing solution with the highest absorbency of carbon dioxide is sprayed to the third washing stage D, where the flue gases flowing into the stage have only a little carbon dioxide left as a result of the carbon dioxide absorption taken place in the previous washing stages. The sodium bicarbonate containing washing solution used in the second and third washing stages flows downwards to the first washing stage, where due to the additional absorption of carbon dioxide the sodium bicarbonate concentration of the solution rises further in the lowest, first washing stage B. When the sodium bicarbonate concentration is high enough, a part of the sodium bicarbonate crystallizes in the solution.

Thus the solution accumulated in the lower part of the flue gas scrubber 1 contains sodium carbonate and sodium bicarbonate in solution form, as well as crystalline sodium bicarbonate. This solution is led with a pump 8 via line 7 to the separator 11. Before the separator 11 a line 29 is connected to the line 7, via which line the solution is recycled back to the first washing stage B. The separator 11 processes the sodium bicarbonate slurry and divides it into two fractions. The first fraction contains substantially all the sodium bicarbonate crystals formed in the scrubber, as well as sodium bicarbonate and sodium carbonate solution, and the second fraction comprises solution, which contains sodium carbonate and sodium bicarbonate. The first fraction separated in the separator 11 is led with a pump 13 via line 14 to a heat exchanger 15. From the heat exchanger 15 the first fraction is led via line 16 to be processed in a stripper 17.
The sodium carbonate solution received from the stripper 17 is led via line 19 to be cooled in the heat exchanger 15. A pump 20 arranged in line 19 is utilized in transferring the solution. From the heat exchanger 15 the sodium carbonate solution is led via line 18 as washing solution to the third washing solution D of the flue gas scrubber 1.

Sodium carbonate solution is also led via line 27 to the separator 11. The addition of sodium carbonate in the separating stage causes the formation of sodium bicarbonate crystals to continue further in the separator.

The solution composed of the second fraction separated in the separator 11 and the sodium carbonate solution received from the stripper 17 and added to the separator is led via line 28 as washing solution to the second washing stage C of the scrubber 1.

Figure 3 shows an embodiment of the invention, where an additional washing stage E is arranged in the scrubber before the first washing stage 1b in the flow direction of the flue gases. The purpose of the additional washing stage is to remove from the flue gases the sulphur oxides disturbing the recovery of carbon dioxide before the recovery of carbon dioxide. In this washing stage the sodium carbonate solution received from the stripper is used as washing solution.

The reaction of sulphur dioxide \((\text{SO}_2)\) with sodium carbonate \((\text{Na}_2\text{CO}_3)\) is as follows:

\[
\text{SO}_2 + \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{SO}_3 + \text{CO}_2 \quad (1)
\]

The sodium sulphite \((\text{Na}_2\text{SO}_3)\) received from the additional washing stage E can be oxidized later into sodium sulphate. Some sodium bisulphite \((\text{Na}_2\text{HSO}_3)\) is also received as a result of the additional washing stage, which can also be oxidized later into sodium sulphate. Sodium sulphate can be removed from the process, for example, to the wastewater treatment of the plant or to practical use. If the reagent
used in the scrubber is a potassium reagent, i.e. potassium carbonate, potassium sulphite (K$_2$SO$_3$) is formed in the reaction with the sulphur dioxides of the flue gases.

The additional washing stage E contains nozzles 2e distributing washing solution and pipes 3e distributing the washing solution and connected to the nozzles. There are several nozzles 2e and they are arranged at even intervals over the cross-sectional area of the scrubber so that they spray washing solution substantially evenly over the entire cross-sectional area of the scrubber.

The flue gases are washed in the additional washing stage E with sodium carbonate solution sprayed via nozzles 2e. The sodium carbonate solution is formed in the stripper 17 and it is led from the heat exchanger 15 via line 30 to a line 31 that recycles washing solution from the bottom of the scrubber to the nozzles 2e of the additional washing stage. A pump 32 arranged in line 31 is utilized in transferring the solution. The sodium carbonate reacts with the sulphur dioxide (SO$_2$) in the flue gases and forms a sodium sulphite and sodium bisulphite containing solution, which is not only recycled to the nozzles 2e, but also removed from the line 31 via a line 33 connected to it.

When the sulphur dioxide has been removed from the flue gases in the additional washing stage E, they flow upwards in the scrubber to the first washing stage B and from there further to the second and third washing stages C and D, which stages aim to recover carbon dioxide. The operation of the first, second and third washing stages B, C, D has already been described above. The cleaned flue gases are led out via a stack 13 arranged in the upper end of the scrubber.

The invention is not intended to be limited to the embodiments presented as examples above, but the invention is intended to be applied widely within the scope of the inventive idea as defined in the appended claims. The heat exchanger used in applying the invention can be any heat exchanger suitable for indirect heating/cooling.
Claims

1. A method for recovering carbon dioxide (CO₂) from flue gases, in which method the flue gases are washed at least with alkali metal carbonate containing washing solution in a scrubber (1), which scrubber (1) contains at least one washing stage (A, B, C, D, E), in which case an alkali metal bicarbonate containing solution is formed as a result of washing, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is increased to such a high level that alkali metal bicarbonate slurry containing crystalline alkali metal bicarbonate is formed.

2. The method according to claim 1, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is increased by absorbing carbon dioxide into the solution.

3. The method according to claim 1 or 2, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is increased by recycling alkali metal bicarbonate containing solution in the scrubber (1).

4. The method according to claim 1, characterized in that the alkali metal bicarbonate slurry is led to a separator (11), which divides the alkali metal bicarbonate slurry into a first and a second fraction, which first fraction contains substantially all the alkali metal bicarbonate crystals formed in the scrubber as well as alkali metal bicarbonate solution, and which second fraction comprises alkali metal carbonate and alkali metal bicarbonate solution.

5. The method according to claim 4, characterized in that the first fraction separated in the separator (11) is led to a stripper (17) where it is processed in order to form a solution containing alkali metal carbonate and carbon dioxide gas.
6. The method according to claim 5, characterized in that alkali metal carbonate solution formed in the stripper (17) is led to at least one washing stage (A, D, E) of the scrubber (1).

7. The method according to claim 5, characterized in that alkali metal carbonate solution formed in the stripper (17) is led to the separator (11).

8. The method according to claim 5, characterized in that the first fraction is processed in the stripper (17) with steam.

9. The method according to claim 1, characterized in that alkali metal hydroxide solution is led to at least one washing stage (A, D) in order to form alkali metal carbonate solution.

10. The method according to claim 5, characterized in that the first fraction is heated with at least one heat exchanger (15) before it is led to the stripper (17).

11. The method according to claim 5, characterized in that alkali metal carbonate solution is cooled with at least one heat exchanger (15) before it is led to the scrubber (1) or the separator (11).

12. The method according to claim 1 or 5, characterized in that the scrubber (1) contains three washing stages, a first washing stage (B), a second washing stage (C) and a third washing stage (D), which are arranged in relation to the height of the scrubber (1) so that the first washing stage (B) is located the lowest in the scrubber (1), the second washing stage (C) is located after the first washing stage (B) and the third washing stage (D) is located uppermost in the scrubber (1), and that the alkali metal carbonate solution formed in the stripper (17) is led to the third washing stage (D).

13. The method according to claim 4 or 12, characterized in that the second fraction separated in the separator (11) is led to the second washing stage (C) of the scrubber (1).
14. The method according to claim 1, characterized in that the alkali metal is selected from a group containing sodium and potassium.

15. The method according to claim 1, characterized in that the flue gases are flue gases containing sulphur oxides.

16. The method according to claim 1 or 15, characterized in that the scrubber (1) contains an additional washing stage (E) for removing the sulphur oxides from the flue gases and that the alkali metal carbonate solution formed in the stripper (17) is led to an additional washing stage (E).

17. An apparatus for recovering carbon dioxide (CO₂) from flue gases, which apparatus contains a scrubber (1) for washing flue gases, which scrubber (1) contains at least one washing stage (A, B, C, D, E), which comprises nozzles (2a, 2b, 2c, 2d, 2e) for spraying washing solution containing at least alkali metal carbonate to flue gases, in which case a solution containing at least alkali metal bicarbonate is formed as a result of washing, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is arranged to be increased to such a high level that alkali metal bicarbonate slurry containing crystalline alkali metal bicarbonate is formed.

18. The apparatus according to claim 17, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is arranged to be increased by absorbing carbon dioxide into the solution.

19. The apparatus according to claim 17, characterized in that the alkali metal bicarbonate concentration of the alkali metal bicarbonate containing solution is arranged to be increased by recycling the alkali metal bicarbonate containing solution in the scrubber (1).

20. The apparatus according to claim 17, characterized in that the apparatus comprises a separator (11), to which the alkali metal bicar-
bonate slurry is arranged to be led to be divided into a first and a second fraction, which first fraction contains substantially all the alkali metal bicarbonate crystals formed in the scrubber as well as alkali metal bicarbonate solution, and which second fraction comprises alkali metal carbonate and alkali metal bicarbonate solution.

21. The apparatus according to claim 20, characterized in that the apparatus comprises a stripper (17) to which the first fraction separated in the separator (11) is arranged to be led to form a solution containing alkali metal carbonate and carbon dioxide gas.

22. The apparatus according to claim 21, characterized in that alkali metal carbonate solution formed in the stripper (17) is arranged to be led to at least one washing stage (A, D, E) of the scrubber (1).

23. The apparatus according to claim 21, characterized in that alkali metal carbonate solution formed in the stripper (17) is arranged to be led to the separator (11).

24. The apparatus according to claim 21, characterized in that the first fraction is arranged to be processed in the stripper (17) with steam.

25. The apparatus according to claim 17, characterized in that alkali metal hydroxide solution is arranged to be led to at least one washing stage (A, D) to form alkali metal carbonate solution.

26. The apparatus according to claim 21, characterized in that the apparatus comprises at least one heat exchanger (15) for heating the first fraction before it is led to the stripper (17).

27. The apparatus according to claim 21, characterized in that the apparatus comprises at least one heat exchanger (15) for cooling the alkali metal carbonate solution before it is led to the scrubber (1) or the separator (11).
28. The apparatus according to claim 17 or 21, characterized in that
the scrubber (1) contains three washing stages, a first washing stage
(B), a second washing stage (C) and a third washing stage (D), which
are arranged in relation to the height of the scrubber (1) so that the first
washing stage (B) is located the lowest in the scrubber (1), the second
washing stage (C) is located after the first washing stage (B) and the
third washing stage (D) is located uppermost in the scrubber (1), and
that alkali metal carbonate solution formed in the stripper (17) is ar-
ranged to be led to the third washing stage (D).

29. The apparatus according to claim 20 or 28, characterized in that
the second fraction separated in the separator (11) is arranged to be
led to the second washing stage (C) of the scrubber (1).

30. The apparatus according to claim 17, characterized in that the al-
kali metal is arranged to be selected from a group containing sodium
and potassium.

31. The apparatus according to claim 17, characterized in that the flue
gases are flue gases containing sulphur oxides.

32. The apparatus according to claim 17 or 31, characterized in that
the scrubber (1) contains an additional washing stage (E) for removing
the sulphur oxides from the flue gases, and that the alkali metal car-
bonate solution formed in the stripper (17) is arranged to be led to the
additional washing stage (E).
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
See extra sheet
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 8: B01D, C01B

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Epo-Internal, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tbody>
<tr>
<td>Y</td>
<td>JP 3038219 A (CHIYODA CHEM ENG CONSTRUCT CO) 19 February 1991 (19.02.1991), PAJ-abstract</td>
<td>1, 2, 14, 9, 15-17, 18, 25, 30-32</td>
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<tr>
<td>Y</td>
<td>the abstract, figure 1</td>
<td>5, 7, 10, 11,</td>
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<tr>
<td>Y</td>
<td>US 4271132 A (EICKMEYER ALLEN G) 02 June 1981 (02.06.1981), column 6, line17-column 7, line 7; claims 1-5; figure 1</td>
<td>5, 6, 8, 10-13, 22, 24, 26-29</td>
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☐ Further documents are listed in the continuation of Box C. ☒ 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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### CLASSIFICATION OF SUBJECT MATTER

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