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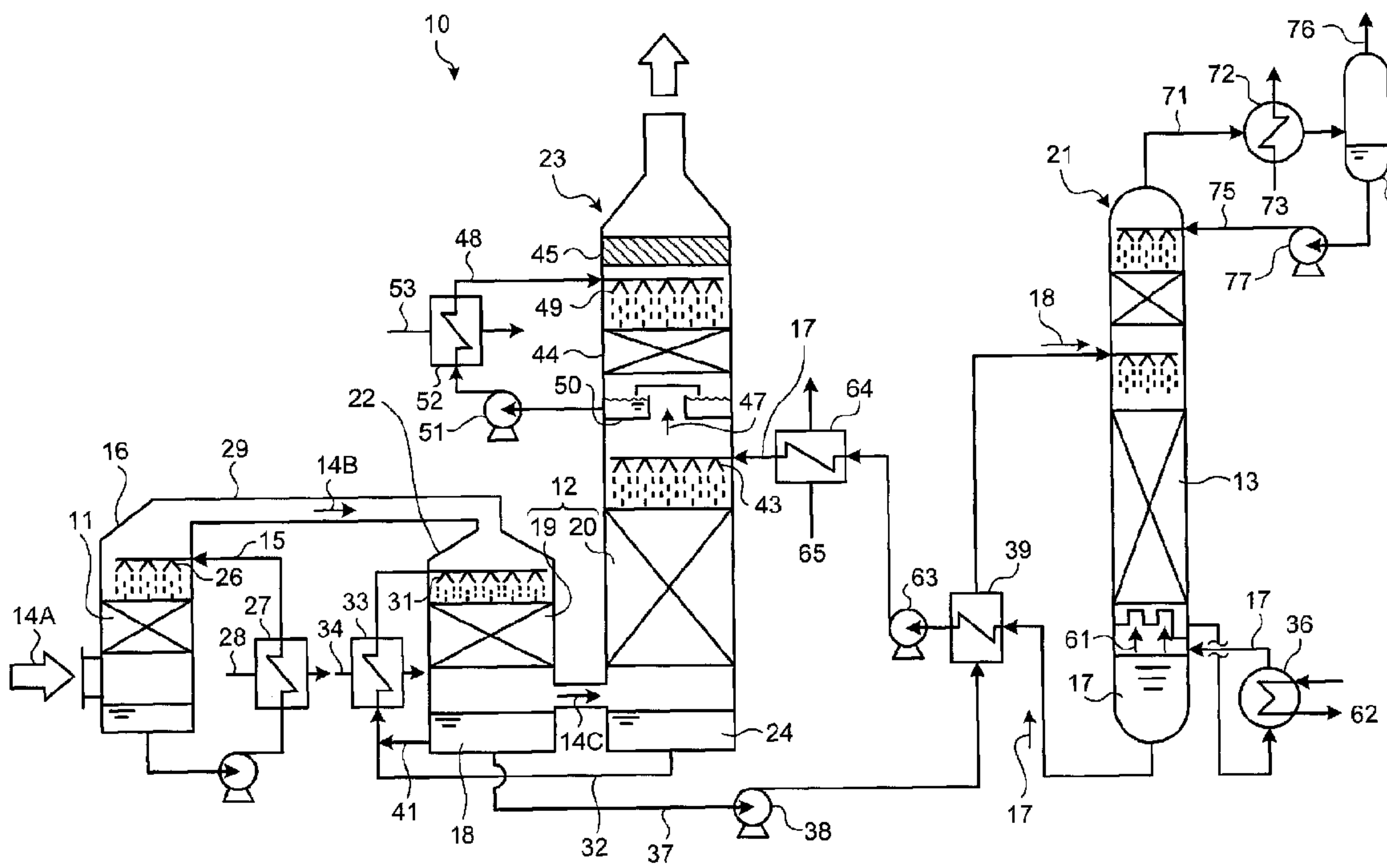


(57) **Abrégé/Abstract:**
A CO_2 recovery device according to one embodiment includes a cooling tower including a cooling unit for bringing flue gas, which contains CO_2, into contact with water so as to cool flue gas; a CO_2-absorbing unit for bringing flue gas into contact with a CO_2 absorbent (lean solution) so as to remove CO_2 from flue gas; and a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent. The CO_2-absorbing unit includes: a cocurrent flow CO_2-absorbing unit provided in a cocurrent flow CO_2 absorber, for bringing flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from flue gas and a countercurrent CO_2-absorbing unit provided in a CO_2 absorber, for bringing flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from flue gas.

ABSTRACT

A CO_2 recovery device according to one embodiment includes a cooling tower including a cooling unit for bringing flue gas, which contains CO_2, into contact with water so as to cool flue gas; a CO_2-absorbing unit for bringing flue gas into contact with a CO_2 absorbent (lean solution) so as to remove CO_2 from flue gas; and a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent. The CO_2-absorbing unit includes: a cocurrent flow CO_2-absorbing unit provided in a cocurrent flow CO_2 absorber, for bringing flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from flue gas and a countercurrent CO_2-absorbing unit provided in a CO_2 absorber, for bringing flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from flue gas.

DESCRIPTION

CO_2 RECOVERY DEVICE

Field

[0001] The present invention relates to a CO_2 recovery device that absorbs CO_2 contained in flue gas.

Background

[0002] Flue gas, which is generated through the combustion of fossil fuel in a boiler of a thermoelectric power plant or the like using a large amount of fossil fuel, contains CO_2. A method of removing and recovering CO_2, which is contained in flue gas, by bringing flue gas, which contains CO_2, into gas-liquid contact with an amine-based CO_2 absorbent in a CO_2 absorber so that CO_2 is absorbed in the CO_2 absorbent, and a method of storing the recovered CO_2 without releasing the recovered CO_2 into the atmosphere have been energetically studied.

[0003] For example, there is used a method of making the CO_2 absorbent absorb CO_2, which is contained in the flue gas, in the CO_2 absorber to remove CO_2 from the flue gas, regenerating the CO_2 absorbent by releasing CO_2, which is absorbed in the CO_2 absorbent, in a regenerator, and reusing the CO_2 absorbent to remove CO_2 from flue gas by circulating the CO_2 absorbent in the CO_2 absorber again (for example, see Patent Literature 1). In this case, the CO_2 absorbent absorbing CO_2 releases CO_2 by being heated with steam in the regenerator. As a result, highly-pure CO_2 is recovered.

Citation List

Patent Literature

[0004] Patent Literature 1: Japanese Laid-open Patent Publication NO. 2008-62165

Summary

[0005] Since a CO_2 recovery device, which uses a method of absorbing, removing, and recovering CO_2 from gas, which contains CO_2, such as flue gas, by using a CO_2 absorbent, is additionally installed on a combustion facility, the operating cost of the CO_2 recovery device should be reduced as much as possible. In particular, much thermal energy is consumed for the release of CO_2 in a regenerator of the CO_2 recovery device. Further, if the consumption of the CO_2 absorbent is large, the amount of a CO_2 absorbent to be additionally supplied is increased. Accordingly, the increase of operating cost is caused.

[0006] For this reason, there is demanded a CO_2 recovery device that improves CO_2 recovery efficiency, reduces the consumption of the CO_2 absorbent, and reduces operating cost when recovering CO_2 from the flue gas.

[0007] Some embodiments of the invention have been made in consideration of the above-mentioned circumstances, and some embodiments of the invention may provide a CO_2 recovery device that efficiently recovers CO_2, reduces the consumption of a CO_2 absorbent, and reduces operating cost.

[0008] According to a first aspect of the present invention, there is provided a CO_2 recovery device including: a cooling unit for bringing flue gas, which contains CO_2, into contact with water so as to cool the flue gas;

a CO_2-absorbing unit for bringing the flue gas into contact with a CO_2 absorbent absorbing CO_2 so as to remove CO_2 from the flue gas; and

an absorbent regenerating unit for releasing CO_2 from the CO_2 absorbent having absorbed CO_2 so as to regenerate the CO_2 absorbent, wherein

the CO_2-absorbing unit includes:

at least one countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas; and

at least one cocurrent flow CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from the flue gas.

[0009] According to a second aspect of the present invention, there is provided the CO_2 recovery device according to the first aspect, wherein the CO_2 absorbent having absorbed CO_2 is cooled in the CO_2-absorbing unit, and is supplied to the CO_2-absorbing unit again.

[0010] According to a third aspect of the present invention, there is provided the CO_2 recovery device according to the first or second aspect, wherein the cocurrent flow CO_2-absorbing unit is provided on the most upstream side in a flow direction of the flue gas.

[0011] According to a fourth aspect of the present invention, there is provided the CO_2 recovery device according to any one of the first to third aspects, wherein the countercurrent CO_2-absorbing unit is provided on the most upstream side in the flow direction of the flue gas.

[0012] According to a fifth aspect of the present invention, there is provided the CO_2 recovery device according to any one of the first to fourth aspects, wherein at least one of the countercurrent CO_2-absorbing unit and the cocurrent flow CO_2-absorbing unit, which are included in the CO_2-absorbing unit, is provided in a CO_2 absorber for bringing the flue gas into contact with the CO_2 absorbent so as to remove CO_2 from the flue gas, and the cocurrent flow CO_2-absorbing unit is provided between the cooling unit and the CO_2 absorber.

[0013] According to a sixth aspect of the present invention, there is provided the CO_2 recovery device according to any one of the first to fifth aspects, wherein at least one of the countercurrent CO_2-absorbing unit and the cocurrent flow CO_2-absorbing unit, which are included in the CO_2-absorbing unit, is provided in the CO_2 absorber for bringing the flue gas into contact with the CO_2 absorbent so as to remove CO_2 from the flue gas, and the countercurrent CO_2-absorbing unit is provided between the cooling unit and the CO_2 absorber.

[0014] According to a seventh aspect of the present invention, there is provided the CO_2 recovery device according to any one of the first to sixth aspects, wherein the cooling unit is provided in a cooling tower for bringing the flue gas into contact with water so as to cool the flue gas, and the countercurrent CO_2-absorbing unit is provided in the cooling tower.

[0014a] According to one aspect of the present invention, there is provided a CO_2 recovery device comprising: a cooling tower including a cooling unit for bringing the flue gas, which contains CO_2, into contact with water so as to cool flue gas; a CO_2 absorber including a CO_2-absorbing unit for bringing the flue gas into contact with a CO_2 absorbent absorbing CO_2 so as to remove CO_2 from the flue gas; and a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent as a lean solution, the rich solution being the CO_2 absorbent having absorbed CO_2 and the lean solution being reused in the CO_2-absorbing unit; wherein the CO_2 recovery device further comprising: at least one countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the

at least one countercurrent CO_2-absorbing unit being provided in the CO_2 absorber; a cocurrent flow CO_2 absorber including at least one cocurrent flow CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from the flue gas, the cocurrent flow CO_2 absorber being provided upstream of the CO_2 absorber; a semi-rich solution extraction line for supplying a semi-rich solution to a flue gas introduction side of the at least one cocurrent flow CO_2-absorbing unit, the semi-rich solution being a solution that has absorbed CO_2 and is stored in a bottom of at least one countercurrent CO_2-absorbing unit; and a rich solution feed line for supplying a rich solution to the regenerator, the rich solution being stored in a bottom of the cocurrent flow CO_2 absorber.

[0014b] According to another aspect of the present invention, there is provided a CO_2 recovery device comprising: a cooling tower including a cooling unit for bringing the flue gas, which contains CO_2, into contact with water so as to cool flue gas; a CO_2 absorber including a CO_2-absorbing unit for bringing the flue gas into contact with a CO_2 absorbent absorbing CO_2 so as to remove CO_2 from the flue gas; and a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent as a lean solution, the rich solution being the CO_2 absorbent having absorbed CO_2 and the lean solution being reused in the CO_2-absorbing unit; wherein the CO_2 recovery device further comprising: at least one countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the at least one countercurrent CO_2-absorbing unit being provided

in the CO_2 absorber; a cocurrent flow CO_2 absorber including at least one cocurrent flow CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from the flue gas, the cocurrent flow CO_2 absorber being provided upstream of the CO_2 absorber; a semi-rich solution extraction line for supplying a semi-rich solution to a flue gas introduction side of the at least one cocurrent flow CO_2-absorbing unit, the semi-rich solution being a solution that has absorbed CO_2 and is stored in a bottom of at least one countercurrent CO_2-absorbing unit; a countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the countercurrent CO_2-absorbing unit being provided on downstream side of the cooling unit in the cooling tower; a rich solution feed line for supplying a rich solution to a top side of the countercurrent CO_2-absorbing unit in the cooling tower, the rich solution being a solution that has absorbed CO_2 in the at least one cocurrent flow CO_2-absorbing unit and is stored in a bottom of the at least one cocurrent flow CO_2-absorbing unit; and a rich solution feed line for supplying a rich solution to the regenerator, the rich solution being a solution that has absorbed in the countercurrent CO_2-absorbing unit and stored in a receiving unit of the countercurrent CO_2-absorbing unit.

[0015] According to the CO_2 recovery device of some embodiments of the invention, it may be possible to efficiently recover CO_2, to reduce the consumption of a CO_2 absorbent, and to reduce operating cost.

Brief Description of Drawings

[0016] FIG. 1 is a diagram simply illustrating the structure of a CO_2 recovery device according to a first embodiment of the invention.

FIG. 2 is a diagram simply illustrating another structure of the CO_2 recovery device according to the first embodiment of the invention.

FIG. 3 is a diagram simply illustrating a part of the structure of a CO_2 recovery device according to a second embodiment of the invention.

FIG. 4 is a diagram illustrating a relation between the filling height of a cocurrent flow CO_2-absorbing unit of a cocurrent flow CO_2 absorber and the reduction rate of the amount of steam that is consumed by a reboiler.

FIG. 5 is a diagram illustrating a relation between a reflux ratio of a semi-rich solution where a semi-rich solution is circulated again in the cocurrent flow CO_2 absorber and the reduction rate of the amount of steam that is consumed by the reboiler.

FIG. 6 is a diagram illustrating a relation between a cross-section ratio of the cocurrent flow CO_2 absorber and the reduction rate of the amount of steam that is consumed by the reboiler.

FIG. 7 is a diagram illustrating a relation between a case where a cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit and the filling height of the cocurrent flow CO_2-absorbing unit are changed, and the reduction rate of the amount of steam that is consumed by the reboiler.

FIG. 8 is a diagram illustrating a relation between the filling height of the cocurrent flow CO_2-absorbing unit of the cocurrent flow CO_2 absorber and the reduction rate of the amount of steam that is consumed by the reboiler.

FIG. 9 is a diagram illustrating a relation between the filling height of a countercurrent CO_2-absorbing unit and the reduction rate of the amount of steam that is consumed by the reboiler.

Description of Embodiments

[0017] The invention will be described in detail below with reference to the drawings. Meanwhile, the invention is not limited by the following forms that embody the invention (hereinafter, referred to as embodiments). Further, components of the following embodiments include components that can be easily supposed by those skilled in the art and substantially the same components, that is, components corresponding to a so-called equivalent range. Furthermore, components disclosed in the following embodiments may be appropriately combined with each other.

[0018] [First embodiment]

A CO_2 recovery device according to a first embodiment of the invention will be described with reference to the drawings. FIG. 1 is a diagram simply illustrating the structure of a CO_2 recovery device according to the first embodiment of the invention. As illustrated in FIG. 1, the CO_2 recovery device 10 according to this embodiment includes a cooling unit 11, a CO_2-absorbing unit 12, and an absorbent regenerating unit 13. The cooling unit 11 cools flue gas 14A by bringing the flue gas 14A containing CO_2 into contact with water 15, and is provided in a cooling tower 16. Further, the CO_2-absorbing unit 12 removes CO_2 from flue gas 14B by bringing the flue gas 14B into contact with a CO_2 absorbent (lean solution) 17 which absorbs CO_2. In this embodiment, the CO_2-absorbing unit 12 includes a cocurrent flow CO_2-absorbing unit 19 that removes CO_2 from the flue gas 14B by bringing the flue gas 14B into contact with a CO_2 absorbent (semi-rich solution) 24, which has absorbed CO_2, in a cocurrent flow, and a countercurrent CO_2-absorbing unit 20 that removes CO_2 from flue gas 14C by bringing the flue gas 14C into contact with the CO_2 absorbent 17 in a countercurrent flow. Furthermore, the absorbent regenerating unit 13 regenerates the CO_2 absorbent 17 by releasing CO_2 from a rich solution 18, and is provided in an absorbent regenerator (hereinafter, referred to as a regenerator) 21.

[0019] In this embodiment, the cocurrent flow CO_2-absorbing unit 19 is provided in a cocurrent flow CO_2 absorber 22 and the countercurrent CO_2-absorbing unit 20 is provided in a CO_2 absorber 23.

[0020] In this embodiment, the CO_2-absorbing unit 12 includes one cocurrent flow CO_2-absorbing unit 19 and one countercurrent CO_2-absorbing unit 20. However, the CO_2-absorbing unit 12 may include a plurality of cocurrent flow CO_2-absorbing units 19 and one countercurrent CO_2-absorbing unit 20, may include one cocurrent flow CO_2-absorbing unit 19 and a plurality of countercurrent CO_2-absorbing units 20, or may include a plurality of cocurrent flow CO_2-absorbing units 19 and a plurality of countercurrent CO_2-absorbing units 20.

[0021] In the CO_2 recovery device 10, the CO_2 absorbent 17, which absorbs CO_2 contained in the flue gas 14A, circulates among the cocurrent flow CO_2 absorber 22, the CO_2 absorber 23, and the regenerator 21 (hereinafter, referred to as "in a system"). In this embodiment, the rich solution 18, which has absorbed CO_2 contained in the flue gas 14B, is fed to the regenerator 21 from the cocurrent flow CO_2 absorber 22. The CO_2 absorbent (lean solution) 17, which is regenerated by removing almost all of CO_2 from the rich solution 18 in the regenerator 21, is fed to the CO_2 absorber 23 from the regenerator 21. The CO_2 absorbent (semi-rich solution) 24, which has absorbed CO_2 remaining in the flue gas 14C, is fed to the cocurrent flow CO_2 absorber 22 from the CO_2 absorber 23.

[0022] The flue gas 14A is gas that contains CO_2 discharged from industrial equipment, such as a boiler or a gas turbine. After the pressure of the flue gas 14A is increased by a flue gas blower or the like, the flue gas 14A is sent to the cooling tower 16.

[0023] The cooling tower 16 is a tower that cools the flue gas 14A by water 15. The cooling tower 16 includes spray nozzles 26 that spray the water 15 into the tower, and a cooling unit 11. The flue gas 14A is cooled by coming into counterflow contact with the water 15 sprayed from the spray nozzles 26 in the cooling unit 11 of the cooling tower 16.

[0024] The water 15 of which the temperature has become high by the heat exchange between the water 15 and the flue gas 14A is stored in the bottom of the cooling tower 16. The water 15 stored in the bottom of the cooling tower 16 is extracted from the bottom of the cooling tower 16, and is cooled by exchanging heat with cooling water 28 in a cooler 27. Then, the water 15 is fed to the cooling tower 16. Accordingly, the water 15 is circulated and used to cool the flue gas 14A.

[0025] The cooled flue gas 14B is discharged from the cooling tower 16 through a flue gas duct 29 that connects the cooling tower 16 to the CO_2 absorber 23, and is fed to the CO_2-absorbing unit 12.

[0026] As described above, the CO_2-absorbing unit 12 includes the cocurrent flow CO_2-absorbing unit 19 and the countercurrent CO_2-absorbing unit 20. The flue gas 14B is fed to the cocurrent flow CO_2 absorber 22 including the cocurrent flow CO_2-absorbing unit 19 and the CO_2 absorber 23 including the countercurrent CO_2-absorbing unit 20 in this order.

[0027] The cocurrent flow CO_2 absorber 22 is provided between the cooling tower 16 including the cooling unit 11 and the CO_2 absorber 23. In this embodiment, the cocurrent flow CO_2 absorber 22 including the cocurrent flow CO_2-absorbing unit 19 is provided on the most upstream side in the flow direction of the flue gas 14B flowing in the CO_2-absorbing unit 12. The flue gas 14B discharged from the cooling tower 16 is fed to the cocurrent flow CO_2 absorber 22 through the flue gas duct 29.

[0028] The cocurrent flow CO_2 absorber 22 is a tower that removes CO_2 from the flue gas 14B by bringing the flue gas 14B into contact with the semi-rich solution 24, which is discharged from the CO_2 absorber 23, in a cocurrent flow. The cocurrent flow CO_2 absorber 22 includes spray nozzles 31 and the cocurrent flow CO_2-absorbing unit 19 that are provided in the tower. The spray nozzles 31 spray the semi-rich solution 24 downward. After the semi-rich solution 24 is discharged from the CO_2 absorber 23 through a semi-rich solution extraction line 32 and is cooled by exchanging heat with cooling water 34 in a cooler 33, the semi-rich solution 24 is fed to the cocurrent flow CO_2 absorber 22. Further, the flue gas 14B is supplied from the top of the cocurrent flow CO_2 absorber 22, and flows in the tower toward the bottom of the tower.

[0029] Accordingly, since the semi-rich solution 24 is cooled before being supplied into the cocurrent flow CO_2 absorber 22, the semi-rich solution 24 can further absorb CO_2, which is contained in the flue gas 14B, in the cocurrent flow CO_2 absorber 22. Therefore, it is possible to increase the concentration of CO_2 contained in the rich solution 18 that is stored in the bottom of the cocurrent flow CO_2 absorber 22.

[0030] Further, since the semi-rich solution 24 is cooled before being supplied into the cocurrent flow CO_2 absorber 22, the semi-rich solution 24 can lower the temperature of the flue gas 14C fed to the CO_2 absorber 23 by coming into contact with the flue gas 14B. For this reason, as described below, it is possible to increase the absorption amount of CO_2, which is contained in the flue gas 14C, even in the CO_2 absorber 23. Accordingly, it is possible to improve the absorption efficiency of CO_2. Furthermore, since the temperature of the flue gas 14C fed to the CO_2 absorber 23 is lowered, the steam pressure of the absorbent of the lean solution 17 is reduced. Accordingly, it is possible to reduce the consumption of the absorbent. Moreover, the temperature of the absorbent rises due to the heat of reaction that is generated at the time of absorption of CO_2, but the flue gas 14C is cooled on the upstream side of the CO_2 absorber 23. Accordingly, the rise of the temperature of the absorbent is also suppressed, so that it is possible to suppress the degradation of the absorbent.

[0031] Further, in a CO_2 recovery device in the related art, a cooling tower 16 and a CO_2 absorber 23 have been connected to each other by a flue gas duct 29. In contrast, the CO_2 recovery device 10 according to this embodiment is provided with the cocurrent flow CO_2 absorber 22 on the flue gas duct 29. Accordingly, according to the CO_2 recovery device 10 of this embodiment, it is possible to effectively use an installation area since the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29 of the CO_2 recovery device that has been already provided in the related art.

[0032] When the cross-sectional area of the cocurrent flow CO_2-absorbing unit 19 is denoted by S1 and the cross-sectional area of the countercurrent CO_2-absorbing unit 20 is denoted by S2, the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is preferably 1.0 or less, more preferably 0.8 or less, and still more preferably 0.5 or less. Accordingly, since it is possible to suitably maintain a contact rate between the semi-rich solution 24 and the flue gas 14B in the cocurrent flow CO_2 absorber 22, it is possible to maintain the absorption efficiency of CO_2 that is contained in the flue gas 14B. As a result, it is possible to reduce the amount of steam that is consumed by a regenerating superheater (reboiler)

36 of the regenerator 21. Moreover, even though the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is small, it is possible to suitably maintain the contact rate between the semi-rich solution 24 and the flue gas 14B in the cocurrent flow CO_2 absorber 22 by increasing the filling height of the cocurrent flow CO_2-absorbing unit 19 as much as that. Therefore, it is possible to maintain the absorption efficiency of CO_2 that is contained in the flue gas 14B.

[0033] Further, the semi-rich solution 24 is previously cooled in the cooler 33 before being supplied to the cocurrent flow CO_2 absorber 22. However, when the semi-rich solution 24 does not need to be cooled, the semi-rich solution 24 may not be cooled in the cooler 33.

[0034] The flue gas 14C, which comes into gas-liquid contact with the semi-rich solution 24 in the cocurrent flow CO_2 absorber 22, is sent to the CO_2 absorber 23 from the side wall of the bottom of the CO_2 absorber 23.

[0035] Furthermore, the rich solution 18, which has absorbed CO_2 contained in the flue gas 14B in the cocurrent flow CO_2-absorbing unit 19, is stored in the bottom of the cocurrent flow CO_2 absorber 22. The rich solution 18 stored in the bottom of the cocurrent flow CO_2 absorber 22 is extracted from a rich solution feed line 37; is pumped from the bottom of the cocurrent flow CO_2 absorber 22 by a rich solvent pump 38 that is provided outside; exchanges heat with the CO_2 absorbent 17, which is regenerated in the regenerator 21, in a rich/lean solution heat exchanger 39; and is then supplied into the regenerator 21 from the side surface of the regenerator.

[0036] A part of the rich solution 18, which is stored in the bottom of the cocurrent flow CO_2 absorber 22, may be extracted from a rich solution extraction-branch line 41, may be mixed to the semi-rich solution 24, and may circulate in the cocurrent flow CO_2 absorber 22 so as to be used. Accordingly, since the rich solution 18 can remove CO_2 from the flue gas 14B by further absorbing CO_2, which is contained in the flue gas 14B, in the cocurrent flow CO_2 absorber 22, it is possible to further increase the concentration of CO_2 contained in the rich solution 18. As a result, it is possible to reduce the amount of steam that is consumed by the reboiler 36.

[0037] Further, when the flow rate of the semi-rich solution 24, which is supplied to the cocurrent flow CO_2 absorber 22 from the CO_2 absorber 23, is denoted by A1 and the flow rate of the rich solution 18, where the rich solution 18 stored in the cocurrent flow CO_2 absorber 22 is supplied to the cocurrent flow CO_2 absorber 22 through the rich solution extraction-branch line 41, is denoted by A2, a reflux ratio (A2/A1) of the rich solution 18 is preferably in a range of 0 to 3 and more preferably in a range of 0 to 2. Accordingly, it is possible to efficiently absorb CO_2, which is contained in the flue gas 14B, while suitably maintaining the rich solution 18 that is fed to the regenerator 21 and regenerated.

[0038] The CO_2 absorber 23 is a tower that removes CO_2 from the flue gas 14C by bringing the flue gas 14C into contact with the CO_2 absorbent 17. The CO_2 absorber 23 includes the countercurrent CO_2-absorbing unit 20, spray nozzles 43, a water washing unit 44, and a demister 45. The flue gas 14C, which is fed into the CO_2 absorber 23, flows in the tower toward the top of the tower from the bottom of the tower. The spray nozzle 43 is a nozzle that sprays the CO_2 absorbent 17 downward. In this embodiment, the countercurrent CO_2-absorbing unit 20 is provided at the lower portion of the CO_2 absorber 23.

[0039] The flue gas 14C, which rises in the tower, comes into contact with the CO_2 absorbent 17, which contains, for example, a basic amine compound as a base, in a countercurrent flow in the countercurrent CO_2-absorbing unit 20. Accordingly, CO_2 contained in the flue gas 14C is absorbed in the CO_2 absorbent 17.

[0040] The semi-rich solution 24, which has absorbed CO_2 contained in the flue gas 14C in the countercurrent CO_2-absorbing unit 20, is stored in the bottom of the CO_2 absorber 23. As described above, the semi-rich solution 24, which is stored in the bottom of the CO_2 absorber 23, is extracted from the semi-rich solution extraction line 32, is fed to the cocurrent flow CO_2 absorber 22, and absorbs CO_2, which is contained in the flue gas 14B, by coming into contact with the flue gas 14B in a cocurrent flow.

[0041] This embodiment is not limited to a case where the semi-rich solution 24 is fed to the cocurrent flow CO_2 absorber 22, and the semi-rich solution 24 may be mixed to the CO_2 absorbent 17, which is fed to the spray nozzles 43, so as to be used to absorb CO_2, which is contained in the flue gas 14C, in the countercurrent CO_2-absorbing unit 20. Further, the semi-rich solution 24 may be supplied to both the cocurrent flow CO_2 absorber 22 and the countercurrent CO_2-absorbing unit 20.

[0042] Furthermore, the water washing unit 44 and the demister 45 are provided on the downstream side in the CO_2 absorber 23 in the flow direction of the flue gas 14C. In this embodiment, the water washing unit 44 and the demister 45 are provided above the countercurrent CO_2-absorbing unit 20 in the tower. After the CO_2 absorbent 17 contained in CO_2-removed flue gas 47, from which CO_2 has been removed in the countercurrent CO_2-absorbing unit 20, is removed from the CO_2-removed flue gas 47 in the water washing unit 44 and the demister 45, the CO_2-removed flue gas 47 is released to the outside of the system from the top of the CO_2 absorber 23.

[0043] Water 48, which is supplied from the outside, is sprayed in the water washing unit 44 from spray nozzles 49, so that impurities contained in the CO_2-removed flue gas 47 are removed in the water washing unit 44. After the water 48, which is sprayed from the spray nozzles 49, is recovered by a receiving unit 50, is fed to the outside of the tower by a pump 51, and is cooled in a cooler 52 by cooling water 53, the water 48 is fed to the spray nozzles 49 so as to be used while circulating.

[0044] In this embodiment, the CO_2-absorbing unit 12 includes one cocurrent flow CO_2-absorbing unit 19 and one countercurrent CO_2-absorbing unit 20. However, this embodiment is not limited thereto, and the CO_2-absorbing unit 12 may include a plurality of cocurrent flow CO_2-absorbing units 19 and one countercurrent CO_2-absorbing unit 20, may include one cocurrent flow CO_2-absorbing unit 19 and a plurality of countercurrent CO_2-absorbing units 20, or may include a plurality of cocurrent flow CO_2-absorbing units 19 and a plurality of countercurrent CO_2-absorbing units 20.

[0045] In this embodiment, the CO_2 absorber 23 includes one countercurrent CO_2-absorbing unit 20 that is provided therein. However, the CO_2 absorber 23 may include a plurality of cocurrent flow CO_2-absorbing units 19 and one countercurrent CO_2-absorbing unit 20 that are provided therein, may include one cocurrent flow CO_2-absorbing unit 19 and a plurality of countercurrent CO_2-absorbing units 20 that are provided therein, or may include a plurality of cocurrent flow CO_2-absorbing units 19 and a plurality of countercurrent CO_2-absorbing units 20 that are provided therein.

[0046] FIG. 2 is a diagram simply illustrating another structure of the CO_2 recovery device according to this embodiment. The CO_2 absorber 23 may have two stages of countercurrent CO_2-absorbing units 20-1 and 20-2 as illustrated in FIG. 2, or may have three or more stages. If the CO_2 absorber 23 is provided with the countercurrent CO_2-absorbing units 20-1 and 20-2, a semi-rich solution 24B, which has absorbed CO_2 remaining in the flue gas 14C after the lean solution 17 is sprayed from spray nozzles 43-2 and passes through the countercurrent CO_2-absorbing unit 20-2, is stored in a receiving unit 55. Subsequently, after the semi-rich solution 24B, which is stored in the receiving unit 55, is cooled in a cooler 56 by cooling water 57, the semi-rich solution 24B is sprayed from spray nozzles 43-1 and passes through the countercurrent CO_2-absorbing unit 20-1, so that the semi-rich solution 24B is changed into a semi-rich solution 24A. The semi-rich solution 24A is stored in the bottom of the CO_2 absorber 23.

[0047] In this case, this embodiment is not limited to a case where the semi-rich solution 24B, which has absorbed CO_2 in the countercurrent CO_2-absorbing unit 20-2, is supplied to the countercurrent CO_2-absorbing unit 20-1 and the semi-rich solution 24A, which has absorbed CO_2 in the countercurrent CO_2-absorbing unit 20-1, is supplied to the cocurrent flow CO_2-absorbing unit 19. The rich solution 18 that has absorbed CO_2 in the cocurrent flow CO_2-absorbing unit 19, and the semi-rich solutions 24A and 24B that have absorbed CO_2 in the countercurrent CO_2-absorbing units 20-1 and 20-2, respectively, may be supplied to the cocurrent flow CO_2-absorbing unit 19 and any one or both of the countercurrent CO_2-absorbing units 20-1 and 20-2 again after being cooled.

[0048] Further, the rich solution 18, which is stored in the bottom of the cocurrent flow CO_2 absorber 22 as illustrated in FIG. 1, is supplied to the regenerator 21 as described above. The regenerator 21 is a tower that includes the absorbent regenerating unit 13 and regenerates the rich solution 18 as the lean solution 17 by releasing CO_2 from the rich solution 18. The rich solution 18, which is released into the regenerator 21 from the top of the regenerator 21, is heated by steam 61 that is supplied from the bottom of the regenerator 21. The steam 61 is generated by the heat exchange between the lean solution 17 and saturated steam 62 in the regenerating superheater (reboiler) 36. The rich solution 18 absorbs heat by being heated by the steam 61, so that most of CO_2 contained in the rich solution 18 is released. When reaching the bottom of the regenerator 21, the rich solution 18 is changed into the CO_2 absorbent (lean solution) 17 from which almost all CO_2 has been removed.

[0049] After the lean solution 17, which is stored in the bottom of the regenerator 21, is fed as a CO_2 absorbent by a lean solvent pump 63 and is cooled in a lean solvent cooler 64 by the heat exchange with cooling water 65, the lean solution 17 is fed to the CO_2 absorber 23.

[0050] Meanwhile, CO_2 gas 71 containing vapor is released from the top of the regenerator 21. After the CO_2 gas 71 containing vapor is discharged from the top of the regenerator 21, vapor contained in the CO_2 gas 71 is condensed in a condenser 72 by cooling water 73, and water 75 is separated by a separation drum 74. After that, CO_2 gas 76 is released to the outside of the system and is recovered. Further, the water 75, which is separated by the separation drum 74, is supplied to the upper portion of the regenerator 21 by a condensed water circulating pump 77.

[0051] As described above, the CO_2 recovery device 10 according to this embodiment includes the cocurrent flow CO_2 absorber 22 that includes the cocurrent flow CO_2-absorbing unit 19 and is provided between the cooling tower 16 and the CO_2 absorber 23, and uses the semi-rich solution 24, which has absorbed CO_2 contained in the flue gas 14C in the CO_2 absorber 23, as an absorbent that further absorbs CO_2 contained in the flue gas 14B in the cocurrent flow CO_2 absorber 22. Accordingly, it is possible to increase the concentration of CO_2 contained in the rich solution 18 that is stored in the bottom of the cocurrent flow CO_2 absorber 22. Moreover, since the semi-rich solution 24 is previously cooled before being supplied into the cocurrent flow CO_2 absorber 22, it is possible to lower the temperature of the flue gas 14C that is fed to the CO_2 absorber 23. For this reason, it is also possible to increase the absorption amount of CO_2, which is contained in the flue gas 14C, in the CO_2 absorber 23 and to reduce the consumption of the absorbent. In addition, since it is possible to provide the cocurrent flow CO_2 absorber 22 on the flue gas duct 29 of the CO_2 recovery device that has been already provided, it is possible to effectively use an installation area.

[0052] Accordingly, since it is possible to efficiently use steam required for releasing CO_2, which is contained in the CO_2 absorbent 17, in the regenerator 21 without the waste of steam, it is possible to increase the operating efficiency of the CO_2 recovery device 10.

[0053] Meanwhile, the CO_2 recovery device 10 according to this embodiment is adapted so that the countercurrent CO_2-absorbing unit 20 is provided in the CO_2 absorber 23. However, this embodiment is not limited thereto and the countercurrent CO_2-absorbing unit 20 may be provided between the cooling unit 11 and the CO_2 absorber 23.

[0054] The CO_2 recovery device 10 according to this embodiment is not limited to a case where the CO_2 recovery device 10 is applied to recover CO_2 contained in the flue gas 14A, and may be suitably used as a device that brings an ingredient contained in flue gas into gas-liquid contact with liquid such as water, such as flue gas desulphurization equipment.

[0055] [Second embodiment]

A CO_2 recovery device according to a second embodiment of the invention will be described with reference to the drawings. Since the structure of the CO_2 recovery device according to this embodiment is the same as the structure of the above-mentioned CO_2 recovery device illustrated in FIG. 1, a diagram illustrating the structure of the CO_2 recovery device will not be provided and description will be made using only drawings illustrating the structure of a cooling tower and a CO_2 absorber. Meanwhile, the same members as the members of the CO_2 recovery device illustrated in FIGS. 1 and 2 are denoted by the same reference numerals and the description thereof will not be made. Further, a case where two countercurrent CO_2-absorbing units 20 are provided as illustrated in FIG. 2 will be described in this embodiment.

[0056] FIG. 3 is a diagram simply illustrating a part of the structure of the CO_2 recovery device according to the second embodiment of the invention. As illustrated in FIG. 3, the CO_2 recovery device according to this embodiment has a structure where the CO_2 recovery device according to the first embodiment illustrated in FIG. 2 further includes a countercurrent CO_2-absorbing unit 81 provided on the most upstream side in the flow direction of the flue gas 14B. That is, the CO_2 recovery device according to the embodiment includes countercurrent CO_2-absorbing units 20-1 and 20-2 that are provided in the CO_2 absorber 23, the cocurrent flow CO_2 absorber 22 that is provided between the cooling tower 16 and the CO_2 absorber 23, and the countercurrent CO_2-absorbing unit 81 that is provided on the downstream side of the cooling unit 11, which is provided in the cooling tower 16, in the gas flow direction (in an upper portion of the tower).

[0057] The cooling tower 16 includes spray nozzles 82 and the countercurrent CO_2-absorbing unit 81 that are provided therein. The countercurrent CO_2-absorbing unit 81 removes CO_2 from the flue gas 14B by bringing the cooled flue gas 14B into contact with a rich solution 18A, which is discharged from the cocurrent flow CO_2 absorber 22, in a countercurrent flow.

[0058] The spray nozzles 82 spray the rich solution 18A downward. After the rich solution 18A is discharged from the cocurrent flow CO_2 absorber 22 through a rich solution extraction line 83 and is cooled in a cooler 84 by the heat exchange with cooling water 85, the rich solution 18A is fed to the cocurrent flow CO_2 absorber 22.

[0059] The countercurrent CO_2-absorbing unit 81 is provided on the downstream side of the cooling unit 11 in the gas flow direction. In this embodiment, the countercurrent CO_2-absorbing unit 81 is provided above the cooling unit 11 of the cooling tower 16. For this reason, the flue gas 14B, which is cooled in the cooling unit 11 of the cooling tower 16, flows to the countercurrent CO_2-absorbing unit 81.

[0060] After coming into contact with the cooled flue gas 14B in the countercurrent CO_2-absorbing unit 81, the rich solution 18A is stored in a receiving unit 86.

[0061] The flue gas 14B, which is supplied to the countercurrent CO_2-absorbing unit 81, comes into counterflow contact with the rich solution 18A in the countercurrent CO_2-absorbing unit 81. The rich solution 18A absorbs CO_2, which is contained in the flue gas 14B, by coming into counterflow contact with the flue gas 14B in the cocurrent flow CO_2 absorber 22. Accordingly, it is possible to remove CO_2 from the flue gas 14B.

[0062] The rich solution 18A is stored in the receiving unit 86 after coming into contact with the cooled flue gas 14B in the countercurrent CO_2-absorbing unit 81. However, a rich solution 18B, which is stored in the receiving unit 86, is extracted from a rich solution feed line 87, and is supplied to the regenerator 21.

[0063] The CO_2 recovery device according to this embodiment uses the semi-rich solution 24A, which is discharged from the CO_2 absorber 23, as an absorbent that absorbs CO_2 contained in flue gas 14C-1 in the cocurrent flow CO_2 absorber 22. Further, the CO_2 recovery device uses the rich solution 18A, which is discharged from the cocurrent flow CO_2 absorber 22, as an absorbent that further absorbs CO_2 contained in the flue gas 14B in the cooling tower 16. That is, the rich solution 18A is an absorbent that has absorbed CO_2 contained in the flue gas 14C-1 in the cocurrent flow CO_2 absorber 22 and has absorbed CO_2 contained in flue gas 14C-2 in the CO_2 absorber 23. For this reason, it is possible to further increase the concentration of CO_2 contained in the rich solution 18B, which is stored in the receiving unit 86 of the cooling tower 16, by using the rich solution 18A as an absorbent that further absorbs CO_2 contained in the flue gas 14B in the countercurrent CO_2-absorbing unit 81.

[0064] A part of the rich solution 18B, which is stored in the receiving unit 86, may be extracted from a rich solution extraction-branch line 88, may be mixed to the rich solution 18A, and may circulate in the countercurrent CO_2-absorbing unit 81 so as to be used. Accordingly, since the rich solution 18A can remove CO_2 from the flue gas 14B by further absorbing CO_2, which is contained in the flue gas 14B, in the countercurrent CO_2-absorbing unit 81, it is possible to further increase the concentration of CO_2 contained in the rich solution 18B.

[0065] Moreover, as for the flow rate A3 of the rich solution 18A that is supplied to the cooling tower 16 from the cocurrent flow CO_2 absorber 22 and the flow rate A4 of the rich solution 18B, where the rich solution 18B stored in the cooling tower 16 is supplied to the cooling tower 16 through the rich solution extraction-branch line 88, a reflux ratio (A4/A3) of the rich solution 18B is preferably in a range of 0 to 3 and more preferably in a range of 0 to 2. Accordingly, it is possible to absorb CO_2, which is contained in the flue gas 14B, while suitably maintaining the rich solution 18B that is fed to the regenerator 21 and regenerated.

[0066] Further, since the rich solution 18A is cooled before being supplied into the cooling tower 16, the rich solution 18A can lower the temperature of the flue gas 14C-1 fed to the CO_2 absorber 23 by coming into contact with the flue gas 14B. Furthermore, since the semi-rich solution 24A is also cooled before being supplied into the cocurrent flow CO_2 absorber 22, the semi-rich solution 24A also can lower the temperature of the flue gas 14C-2 that is fed to the CO_2 absorber 23. For this reason, it is possible to increase the absorption amount of CO_2, which is contained in the flue gas 14C, in the CO_2 absorber 23. Accordingly, it is possible to improve the absorption efficiency of CO_2 and to reduce the consumption of the absorbent.

[0067] In addition, since the CO_2 recovery device according to this embodiment is provided with the cocurrent flow CO_2 absorber 22 on the flue gas duct 29 of the CO_2 recovery device having been already provided and is provided with the countercurrent CO_2-absorbing unit 81 on the downstream side in the cooling tower 16 in the gas flow direction (in an upper portion of the tower), it is possible to effectively use an installation area.

[0068] As described above, according to the CO_2 recovery device of this embodiment, since it is possible to improve the absorption efficiency of CO_2, which is contained in the flue gas 14A, into a CO_2 absorbent 17 and to reduce the consumption of the absorbent contained in the CO_2 absorbent 17, it is possible to efficiently use the CO_2 absorbent 17. Accordingly, since it is possible to efficiently use steam required for releasing CO_2, which is contained in the CO_2 absorbent 17, in the regenerator 21 without the waste of steam, it is possible to further increase the operating efficiency of the CO_2 recovery device. Further, it is also possible to more effectively apply this embodiment to the device that has been already provided.

[Examples]

[0069] Next, the test results of the reduction rate of the amount of steam, which is consumed by the reboiler when the CO_2 recovery device according to this embodiment is used, will be described.

[0070] <When the cocurrent flow CO_2 absorber was provided between the cooling tower and the CO_2 absorber>

When the cocurrent flow CO_2 absorber 22 was provided between the cooling tower 16 and the CO_2 absorber 23 as in the CO_2 recovery device 10 according to the first embodiment of the invention illustrated in FIG. 1, the reduction rate of the amount of steam consumed by the reboiler 36 was examined in each of a case where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 was changed, a case where the reflux ratio (A2/A1) of the semi-rich solution 24 circulating in the cocurrent flow CO_2 absorber 22 was changed, and a case where the cross-section ratio (S1/S2) between the cocurrent flow CO_2 absorber 22 and the CO_2 absorber 23 was changed. Hereinafter, description will be made with reference to the CO_2 recovery device 10 according to the first embodiment of the invention illustrated in FIG. 1.

[0071] [A relation between the filling height of the countercurrent CO_2-absorbing unit 20 of the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam consumed by the reboiler 36]

FIG. 4 is a diagram illustrating a relation between the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam that is consumed by the reboiler 36. Meanwhile, Comparative Example 1 is a test example where the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100% in a CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22. In Comparative Example 1, the amount of steam consumed by the reboiler 36 was a reference value (0%). Example 1-1 is a test example where the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 is 14% when the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%. Example 1-2 is a test example where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 is 28% when the height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%. Example 1-3 is a test example where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber is 43% when the height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%. In all of Examples 1-1 to 1-3, the reflux ratio (A2/A1) of the rich solution 18 between the flow rate A1 of the semi-rich solution 24, which is supplied to the cocurrent flow CO_2 absorber 22 from the CO_2 absorber 23, and the flow rate A2 of the rich solution 18, where the rich solution 18 stored in the cocurrent flow CO_2 absorber 22 is supplied to the cocurrent flow CO_2 absorber 22 through the rich solution extraction-branch line 41, was 0 and the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 between the cross-sectional area S1 of the cocurrent flow CO_2-absorbing unit 19 and the cross-sectional area S2 of the countercurrent CO_2-absorbing unit 20 was 1.

[0072] As illustrated in FIG. 4, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 was increased. Accordingly, when the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29, it is possible to increase the reduction rate of the amount of steam consumed by the reboiler 36 as the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 is increased.

[0073] [A relation between the reflux ratio (A2/A1) of the semi-rich solution 24 where the semi-rich solution 24 is circulated again in the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam consumed by the reboiler 36]

FIG. 5 is a diagram illustrating a relation between the reflux ratio (A2/A1) of the semi-rich solution 24 where the semi-rich solution 24 is circulated again in the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam that is consumed by the reboiler 36. Meanwhile, Comparative Example 2 is a test example where the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22 as in Comparative Example 1. In Comparative Example 2, the amount of steam consumed by the reboiler 36 was a reference value (0%). Each of Examples 2-1 to 2-3 is a test example where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22, when the height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%, is 28% so that the cross-section ratio (S1/S2) is 1. In Example 2-1, the reflux ratio of the semi-rich solution 24 was 0. In Example 2-2, the reflux ratio of the semi-rich solution 24 was 1. In Example 2-3, the reflux ratio of the semi-rich solution 24 was 2.

[0074] As illustrated in FIG. 5, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as the reflux ratio (A2/A1) of the rich solution 18 circulated in the cocurrent flow CO_2 absorber 22 was increased. Accordingly, when the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29, it is possible to increase the reduction rate of the amount of steam consumed by the reboiler 36 as the reflux ratio of the rich solution 18 circulated in the cocurrent flow CO_2 absorber 22 is increased.

[0075] [A relation between the cross-section ratio of the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam consumed by the reboiler 36]

FIG. 6 is a diagram illustrating a relation between the cross-section ratio of the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam that is consumed by the reboiler 36. Meanwhile, Comparative Example 3 is a test example where the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22 as in Comparative Examples 1 and 2. Each of Examples 3-1 to 3-3 is a test example where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22, when the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%, is 28% so that the reflux ratio (A2/A1) of the rich solution 18 is 0. In Example 3-1, the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 1. In Example 3-2, the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 0.75. In example 3-3, the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 0.5.

[0076] As illustrated in FIG. 6, when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 0.75 or 1, the reduction rate of the amount of steam consumed by the reboiler 36 was large as compared to when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is 0.5. The reduction rate of the amount of steam consumed by the reboiler 36 when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 0.75 was substantially the same as that when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 1.0. Accordingly, when the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29, it is possible to increase the reduction rate of the amount of steam, which is consumed by the reboiler 36, by making the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 larger than 0.5.

[0077] [Influence on the reduction rate of the amount of steam, which is consumed by the reboiler 36, when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 and the filling height of the cocurrent flow CO_2-absorbing unit 19 are changed]

FIG. 7 is a diagram illustrating a relation between a case where the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 and the filling height of the cocurrent flow CO_2-absorbing unit 19 are changed, and the reduction rate of the amount of steam that is consumed by the reboiler 36. Example 3-4 is a test example where the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 is 43%, the reflux ratio (A2/A1) of the rich solution 18 is 0, and the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is 0.5 when the height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100%.

[0078] As illustrated in FIG. 7, when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 0.5, the reduction rate of the amount of steam consumed by the reboiler 36 was small as compared to when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is 1. However, when the filling height of the cocurrent flow CO_2-absorbing unit 19 was increased, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as compared to when the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 1. Accordingly, when the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29 and the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 is small, it is possible to increase the reduction rate of the amount of steam, which is consumed by the reboiler 36, by making the filling height of the cocurrent flow CO_2-absorbing unit 19 high.

[0079] [A relation between the reduction rate of the amount of steam, which is consumed by the reboiler 36, and the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 when the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is formed in two stages]

FIG. 8 is a diagram illustrating a relation between the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 and the reduction rate of the amount of steam that is consumed by the reboiler 36. Meanwhile, Comparative Example 4-1 is a test example where the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22 as in Comparative Example 1. In Comparative Example 4-1, the amount of steam consumed by the reboiler 36 was a reference value (0%). Comparative Example 4-2 is a test example where the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is formed in two stages and the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22. Example 4-1 is a test example where the filling height of the cocurrent flow CO_2-absorbing unit 19 is 14% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Example 4-2 is a test example where the filling height of the cocurrent flow CO_2-

absorbing unit 19 is 28% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Example 4-3 is a test example where the filling height of the cocurrent flow CO_2-absorbing unit 19 is 43% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Further, in all of Examples 4-1 to 4-3 and Comparative Example 4-2, the filling height of the countercurrent CO_2-absorbing unit 20-1 was 29% and the filling height of the countercurrent CO_2-absorbing unit 20-2 was 71%. Furthermore, in all of Examples 4-1 to 4-3 and Comparative Examples 4-1 and 4-2, the reflux ratio (A2/A1) of the rich solution 18 was 0 and the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 1.

[0080] As illustrated in FIG. 8, when the CO_2 absorber 23 included the countercurrent CO_2-absorbing units 20-1 and 20-2 so that the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 was formed in two stages, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as compared to when the CO_2 absorber 23 included the countercurrent CO_2-absorbing unit 20 so that the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 was formed in one stage (see Comparative Examples 4-1 and 4-2). Moreover, when the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 was formed in two stages and the cocurrent flow CO_2 absorber 22 was provided on the flue gas duct 29 as in Example 4-1, the reduction rate of the amount of steam consumed by the reboiler 36 was further increased. Further, as in Examples 4-1 to 4-3, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 was increased. Accordingly, when the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is formed in a plurality of stages and the cocurrent flow CO_2 absorber 22 is provided on the flue gas duct 29, it is possible to further increase the reduction rate of the amount of steam that is consumed by the reboiler 36. Furthermore, it is possible to increase the reduction rate of the amount of steam, which is consumed by the reboiler 36, as the height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 is increased.

[0081] <When the cocurrent flow CO_2 absorber 22 was provided in the cooling tower 16 and between the cooling tower 16 and the CO_2 absorber 23>

[A relation between the filling height of the countercurrent CO_2-absorbing unit 81, which is provided in the cooling tower 16, and the reduction rate of the amount of steam consumed by the reboiler 36 when the CO_2-absorbing unit of the CO_2 absorber 23 is formed in two stages]

FIG. 9 is a diagram illustrating a relation between the filling height of the countercurrent CO_2-absorbing unit 81 and the reduction rate of the amount of steam that is consumed by the reboiler 36. Meanwhile, Comparative Example 5-1 is a test example where the filling height of the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22 as in Comparative Example 4-1. In Comparative Example 5-1, the amount of steam consumed by the reboiler 36 was a reference value (0%). Comparative Example 5-2 is a test example where the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is formed in two stages and the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 is 100% in the CO_2 recovery device in the related art without the cocurrent flow CO_2 absorber 22 as in Comparative Example 4-2. Comparative Example 5-3 is a test example where the sum of the filling heights of the cocurrent flow CO_2-absorbing unit 19 is 14%, the countercurrent CO_2-absorbing unit 20 of the CO_2 absorber 23 is formed in two stages, and the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 is 100% in the CO_2 recovery device including the cocurrent flow CO_2 absorber 22. Example 5-1 is a test example where the filling height of the countercurrent CO_2-absorbing unit 81 is 14% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Example 5-2 is a test example where the filling height of the countercurrent CO_2-absorbing unit 81 is 28% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Example 5-3 is a test example where the filling height of the countercurrent CO_2-absorbing unit 81 is 43% when the sum of the filling heights of the countercurrent CO_2-absorbing units 20-1 and 20-2 of the CO_2 absorber 23 is 100%. Further, in all of Examples 5-1 to 5-3 and Comparative Example 5-2, the filling height of the countercurrent CO_2-absorbing unit 20-1 was 29% and the filling height of the countercurrent CO_2-absorbing unit 20-2 was 71%. Furthermore, in all of Examples 5-1 to 5-3 and Comparative Example 5-3, the filling height of the cocurrent flow CO_2-absorbing unit 19 of the cocurrent flow CO_2 absorber 22 was 28%. Moreover, in all of Examples 5-1 to 5-3 and Comparative Example 5-3, the reflux ratio (A2/A1) of the rich solution 18A was 0 and the cross-section ratio (S1/S2) of the cocurrent flow CO_2-absorbing unit 19 was 1. Further, in each of Examples 5-1 to 5-3, the reflux ratio (A4/A3) of the rich solution 18B between the flow rate A3 of the rich solution 18A, which is supplied to the cooling tower 16 from the cocurrent flow CO_2 absorber 22, and the flow rate A4 of the rich solution 18, where the rich solution 18B stored in the cooling tower 16 was supplied to the cocurrent flow CO_2 absorber 22 through a rich solution extraction-branch line 83, was 0.

[0082] As illustrated in FIG. 9, the reduction rate of the amount of steam consumed by the reboiler 36 was increased when the countercurrent CO_2-absorbing unit 81 was provided in the cooling tower 16 and the cocurrent flow CO_2 absorber 22 was provided between the cooling tower 16 and the CO_2 absorber 23 (see Examples 5-1 to 5-3). Moreover, the reduction rate of the amount of steam consumed by the reboiler 36 was increased as the filling height of the countercurrent CO_2-absorbing unit 81 provided in the cooling tower 16 was increased. Accordingly, it is possible to further increase the reduction rate of the amount of steam, which is consumed by the reboiler 36, by providing the countercurrent CO_2-absorbing unit 81 in the cooling tower 16 and providing the cocurrent flow CO_2 absorber 22 on the flue gas duct 29. Further, it is possible to increase the reduction rate of the amount of steam, which is consumed by the reboiler 36, as the filling height of the countercurrent CO_2-absorbing unit 81 provided in the cooling tower 16 is increased.

Reference Signs List

[0083] 10 CO_2 RECOVERY DEVICE

11 COOLING UNIT

12 CO_2-ABSORBING UNIT

13 ABSORBENT REGENERATING UNIT

14A to 14C, 14C-1, 14C-2 FLUE GAS

15, 48, 75 WATER

16 COOLING TOWER

17 CO_2 ABSORBENT (LEAN SOLUTION)

18, 18A, 18B RICH SOLUTION

19 COCURRENT FLOW CO_2-ABSORBING UNIT

20, 20-1, 20-2, 81 COUNTERCURRENT CO_2-ABSORBING UNIT

21 ABSORBENT REGENERATOR

22 COCURRENT FLOW CO_2 ABSORBER

23 CO_2 ABSORBER

24, 24A, 24B SEMI-RICH SOLUTION

26, 31, 43, 43-1, 43-2, 49, 82 SPRAY NOZZLE

27, 33, 52, 56, 84 COOLER

28, 34, 53, 57, 65, 73, 85 COOLING WATER

29 FLUE GAS DUCT

32 SEMI-RICH SOLUTION EXTRACTION LINE

36 REGENERATING SUPERHEATER (REBOILER)

37, 87 RICH SOLUTION FEED LINE

38 RICH SOLVENT PUMP

39 RICH/LEAN SOLUTION HEAT EXCHANGER

41, 83, 88 RICH SOLUTION EXTRACTION-BRANCH LINE

44 WATER WASHING UNIT

45 DEMISTER

47 CO_2-REMOVED FLUE GAS

50, 55, 86 RECEIVING UNIT

51 PUMP

61 STEAM

62 SATURATED STEAM

63 LEAN SOLVENT PUMP

64 LEAN SOLVENT COOLER

71, 76 CO_2 GAS

72 CONDENSER

74 SEPARATION DRUM

77 CONDENSED WATER CIRCULATING PUMP

CLAIMS:

1. A CO_2 recovery device comprising:

a cooling tower including a cooling unit for bringing the flue gas, which contains CO_2, into contact with water so as to cool flue gas;

a CO_2 absorber including a CO_2-absorbing unit for bringing the flue gas into contact with a CO_2 absorbent absorbing CO_2 so as to remove CO_2 from the flue gas; and

a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent as a lean solution, the rich solution being the CO_2 absorbent having absorbed CO_2 and the lean solution being reused in the CO_2-absorbing unit; wherein

the CO_2 recovery device further comprising:

at least one countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the at least one countercurrent CO_2-absorbing unit being provided in the CO_2 absorber;

a cocurrent flow CO_2 absorber including at least one cocurrent flow CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from the flue gas, the cocurrent flow CO_2 absorber being provided upstream of the CO_2 absorber;

a semi-rich solution extraction line for supplying a semi-rich solution to a flue gas introduction side of the at least one cocurrent flow CO_2-absorbing unit, the semi-rich solution being a solution that has absorbed CO_2 and is stored in a bottom of at least one countercurrent CO_2-absorbing unit; and

a rich solution feed line for supplying a rich solution to the regenerator, the rich solution being stored in a bottom of the cocurrent flow CO_2 absorber.

2. A CO_2 recovery device comprising:

a cooling tower including a cooling unit for bringing the flue gas, which contains CO_2, into contact with water so as to cool flue gas;

a CO_2 absorber including a CO_2-absorbing unit for bringing the flue gas into contact with a CO_2 absorbent absorbing CO_2 so as to remove CO_2 from the flue gas; and

a regenerator including an absorbent regenerating unit for releasing CO_2 from a rich solution so as to regenerate the CO_2 absorbent as a lean solution, the rich solution being the CO_2 absorbent having absorbed CO_2 and the lean solution being reused in the CO_2-absorbing unit; wherein

the CO_2 recovery device further comprising:

at least one countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the at least one countercurrent CO_2-absorbing unit being provided in the CO_2 absorber;

a cocurrent flow CO_2 absorber including at least one cocurrent flow CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a cocurrent flow so as to remove CO_2 from the flue gas, the cocurrent flow CO_2 absorber being provided upstream of the CO_2 absorber;

a semi-rich solution extraction line for supplying a semi-rich solution to a flue gas introduction side of the at least one cocurrent flow CO_2-absorbing unit, the semi-rich solution being a solution that has absorbed CO_2 and is stored in a bottom of at least one countercurrent CO_2-absorbing unit;

a countercurrent CO_2-absorbing unit for bringing the flue gas into contact with the CO_2 absorbent in a countercurrent flow so as to remove CO_2 from the flue gas, the countercurrent CO_2-absorbing unit being provided on downstream side of the cooling unit in the cooling tower;

a rich solution feed line for supplying a rich solution to a top side of the countercurrent CO_2-absorbing unit in the cooling tower, the rich solution being a solution that has absorbed CO_2 in the at least one cocurrent flow CO_2-absorbing unit and is stored in a bottom of the at least one cocurrent flow CO_2-absorbing unit; and

a rich solution feed line for supplying a rich solution to the regenerator, the rich solution being a solution that has absorbed in the countercurrent CO_2-absorbing unit and stored in a receiving unit of the countercurrent CO_2-absorbing unit.

3. The CO_2 recovery device according to claim 1 or 2, further comprising:

a cooler for cooling the semi-rich solution, the cooler being interposed on the semi-rich solution extraction line.

4. The CO_2 recovery device according to any one of claims 1 to 3, wherein

a filling height of the cocurrent flow CO_2-absorbing unit is equal to or less than 43% of a filling height of the countercurrent flow CO_2-absorbing unit of the CO_2 absorber.

5. The CO_2 recovery device according to any one of claims 1 to 4, wherein

a cross-section ratio (S_1/S_2) of S_1 and S_2 is equal to or less than 1.0, the S_1 being a cross-section of the cocurrent flow CO_2-absorbing unit and the S_2 being a cross-section of the countercurrent CO_2-absorbing unit of the CO_2 absorber.

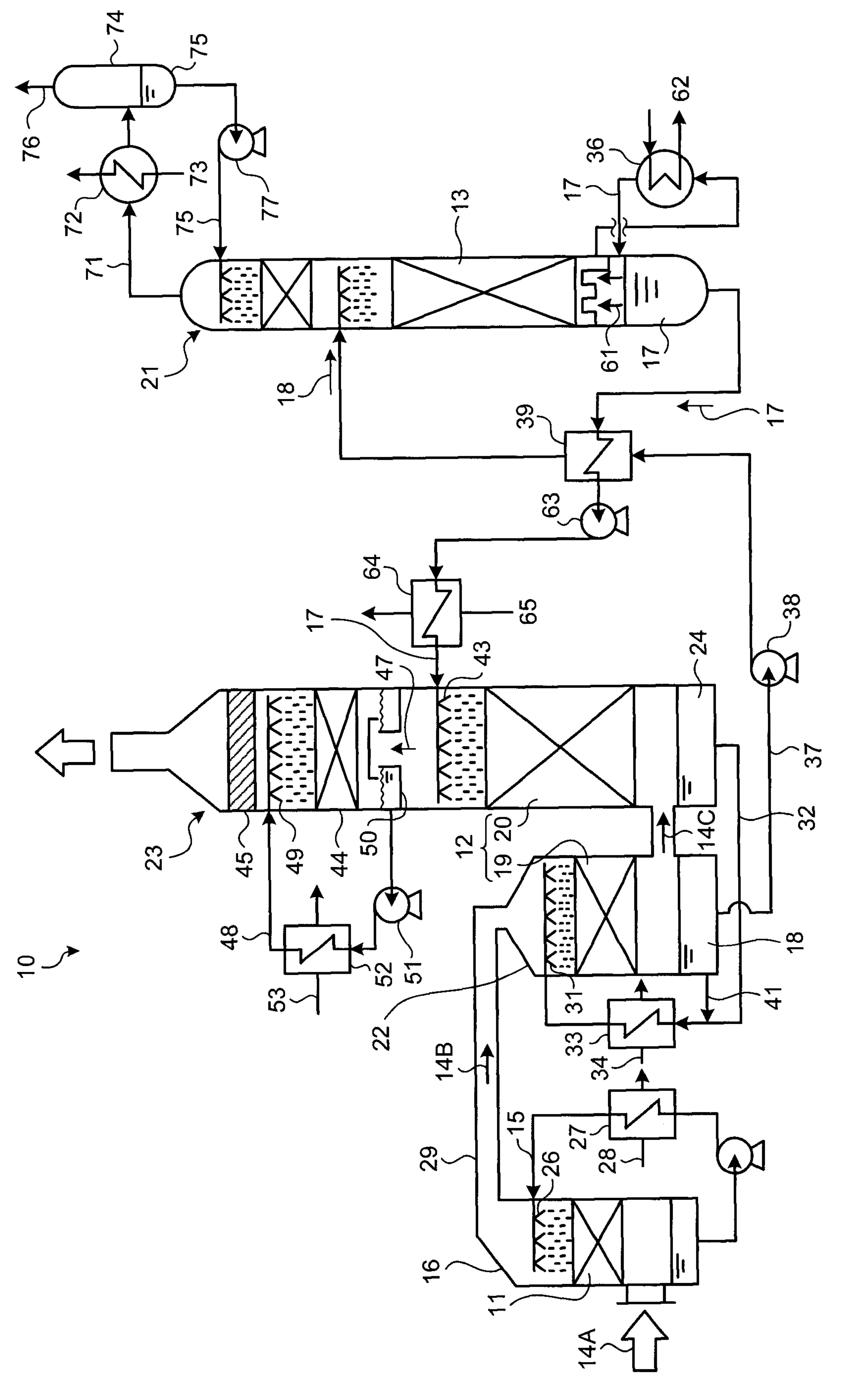


FIG.1

FIG.2

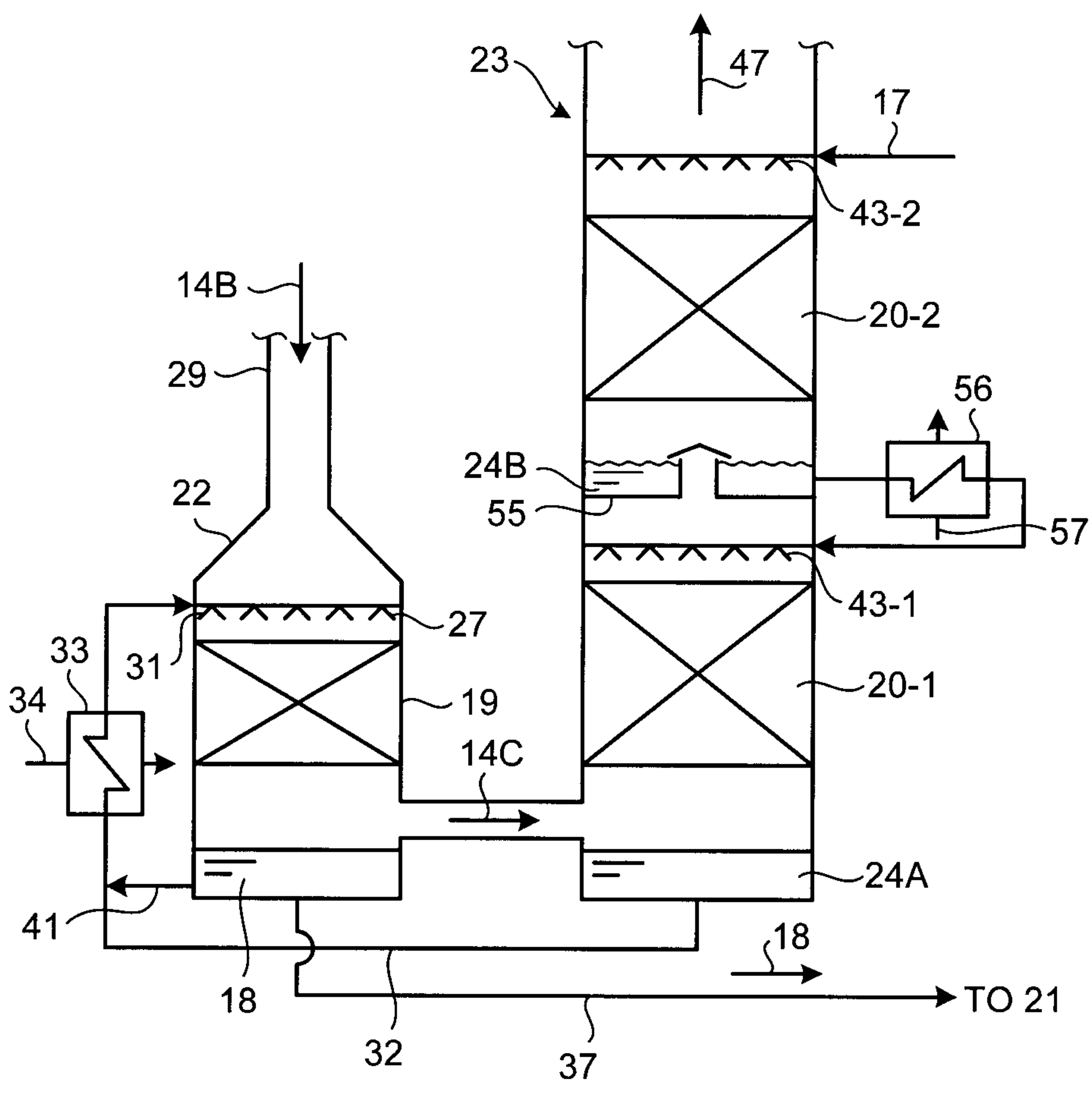

23
47
17
43-2
20-2
14B
29
56
24B
55
57
22
43-1
27
33
31
19
20-1
34
14C
24A
41
18
18
TO 21
32
37

FIG.3

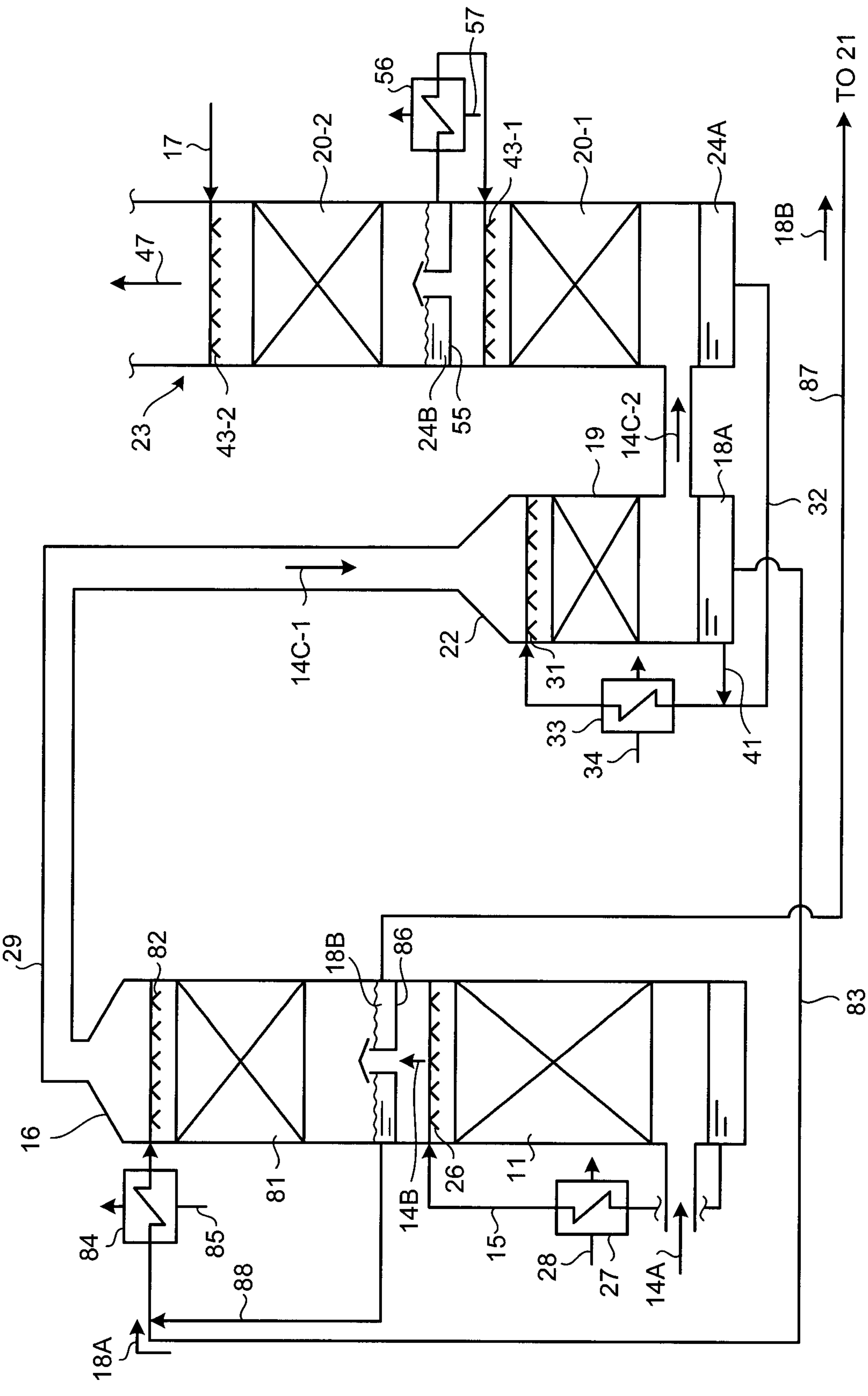

TO 21
17
20-2
56
57
43-1
20-1
24A
47
18B
23
43-2
24B
55
87
14C-2
18A
19
32
14C-1
22
31
33
34
41
29
82
18B
86
83
16
81
14B
26
11
84
85
15
28
27
14A
88
18A

FIG.4

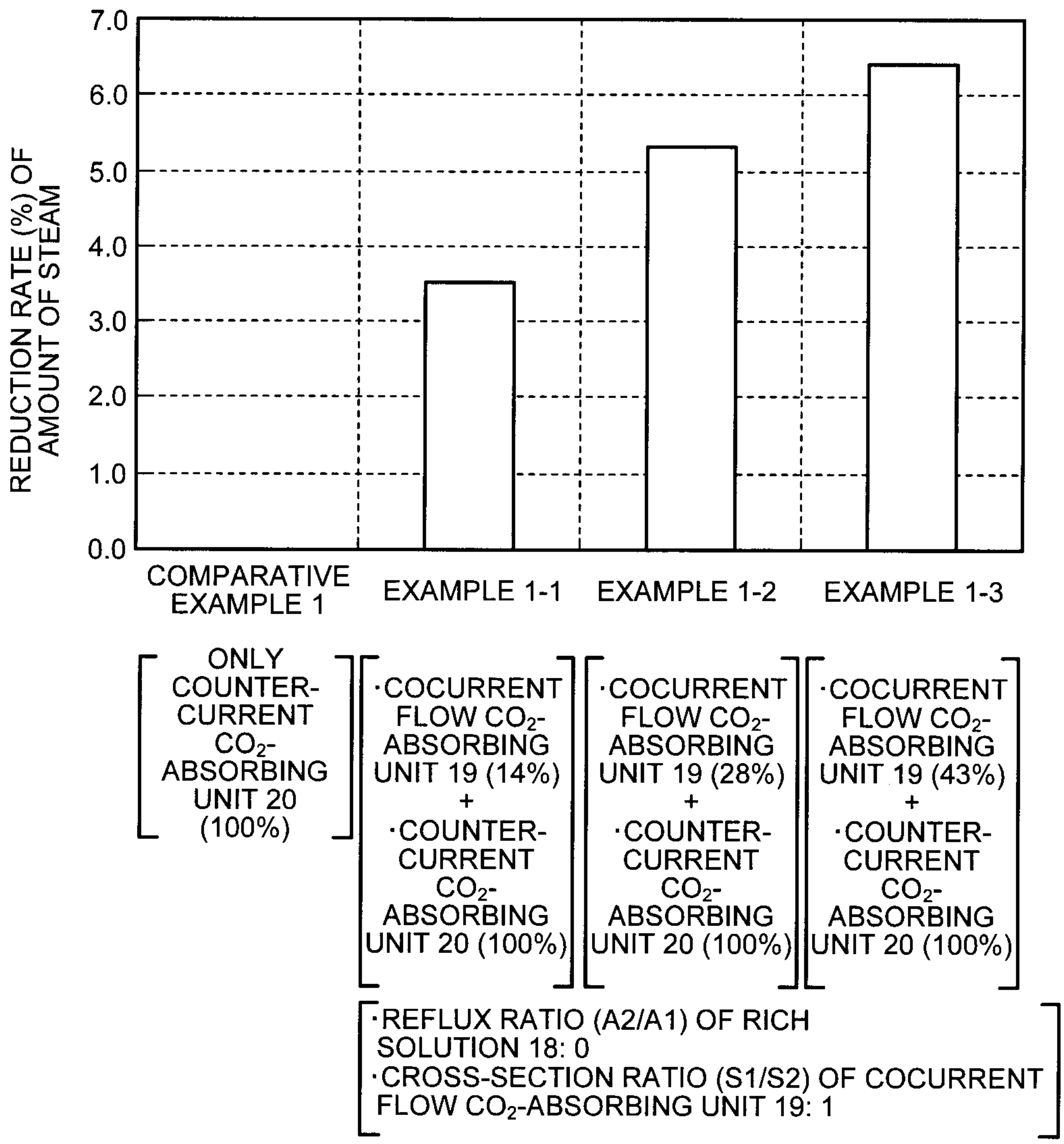

7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
REDUCTION RATE (%) OF AMOUNT OF STEAM
COMPARATIVE EXAMPLE 1
EXAMPLE 1-1
EXAMPLE 1-2
EXAMPLE 1-3
ONLY COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
·COCURRENT FLOW CO_2-ABSORBING UNIT 19 (14%) + ·COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
·COCURRENT FLOW CO_2-ABSORBING UNIT 19 (28%) + ·COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
·COCURRENT FLOW CO_2-ABSORBING UNIT 19 (43%) + ·COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
·REFLUX RATIO (A2/A1) OF RICH SOLUTION 18: 0
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 1

FIG.5

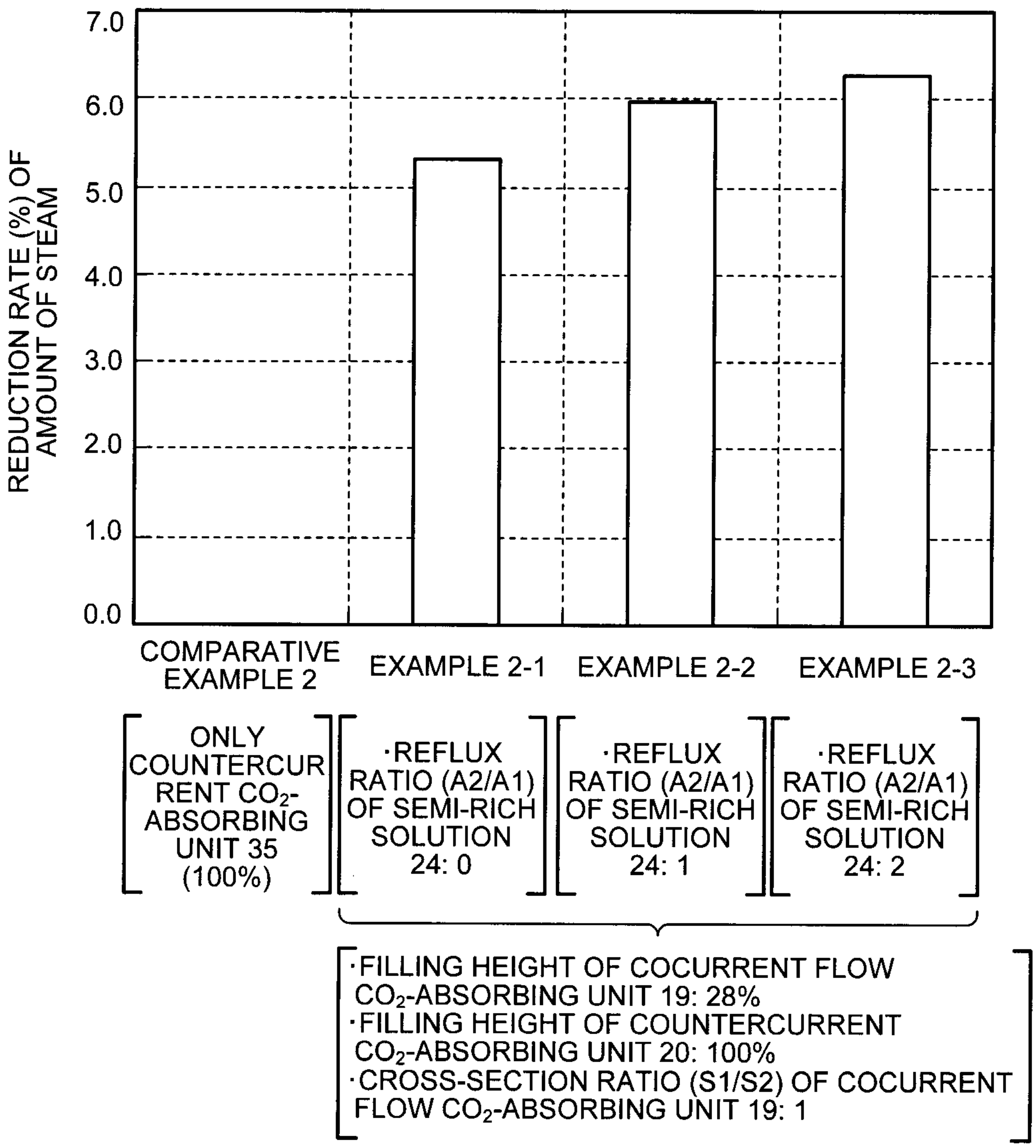

7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
REDUCTION RATE (%) OF AMOUNT OF STEAM
COMPARATIVE EXAMPLE 2
EXAMPLE 2-1
EXAMPLE 2-2
EXAMPLE 2-3
ONLY COUNTERCURRENT CO_2-ABSORBING UNIT 35 (100%)
·REFLUX RATIO (A2/A1) OF SEMI-RICH SOLUTION 24: 0
·REFLUX RATIO (A2/A1) OF SEMI-RICH SOLUTION 24: 1
·REFLUX RATIO (A2/A1) OF SEMI-RICH SOLUTION 24: 2
·FILLING HEIGHT OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 28%
·FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20: 100%
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 1

FIG.6

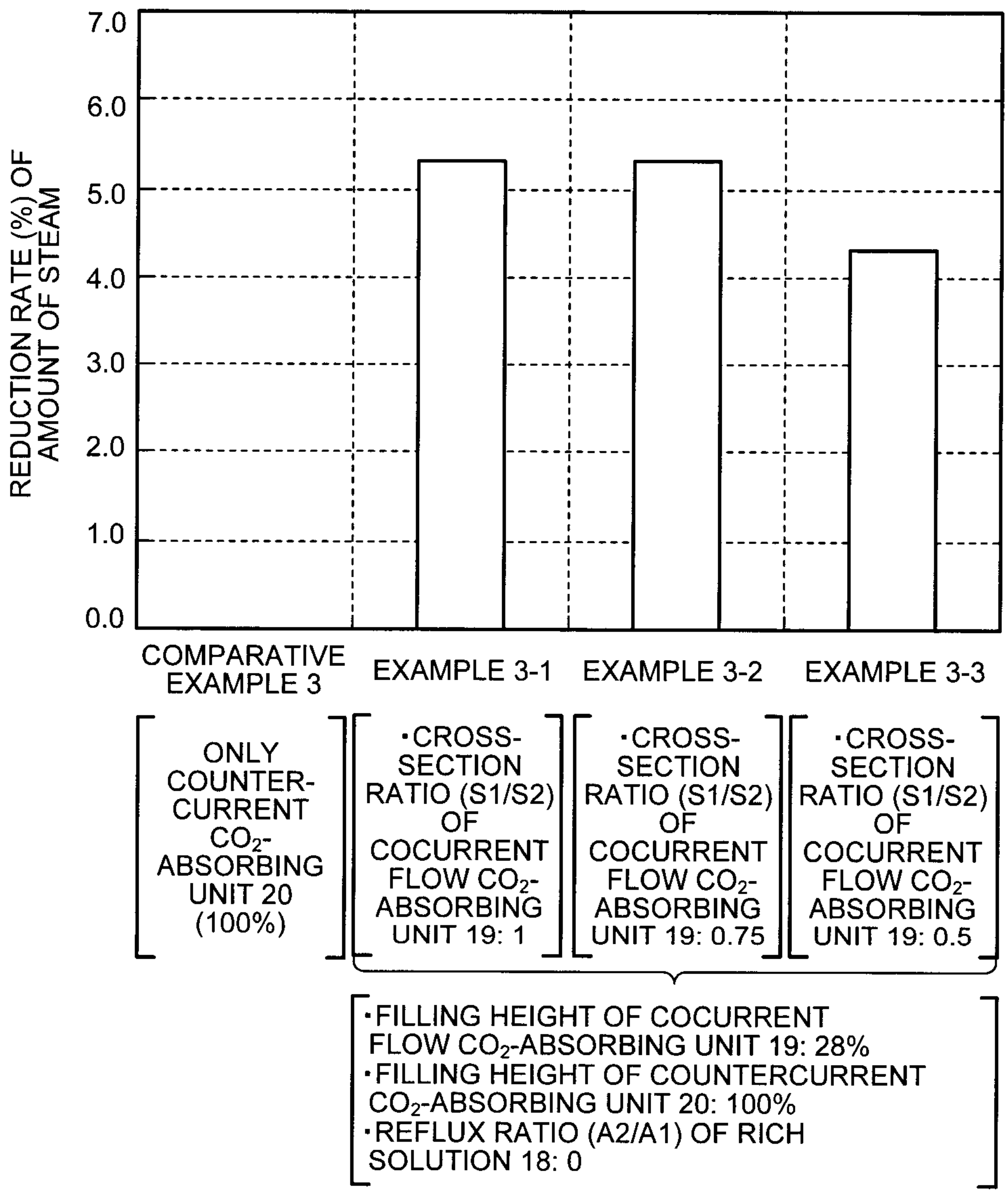

7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
REDUCTION RATE (%) OF AMOUNT OF STEAM
COMPARATIVE EXAMPLE 3
EXAMPLE 3-1
EXAMPLE 3-2
EXAMPLE 3-3
ONLY COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 1
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 0.75
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 0.5
·FILLING HEIGHT OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 28%
·FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20: 100%
·REFLUX RATIO (A2/A1) OF RICH SOLUTION 18: 0

FIG.7

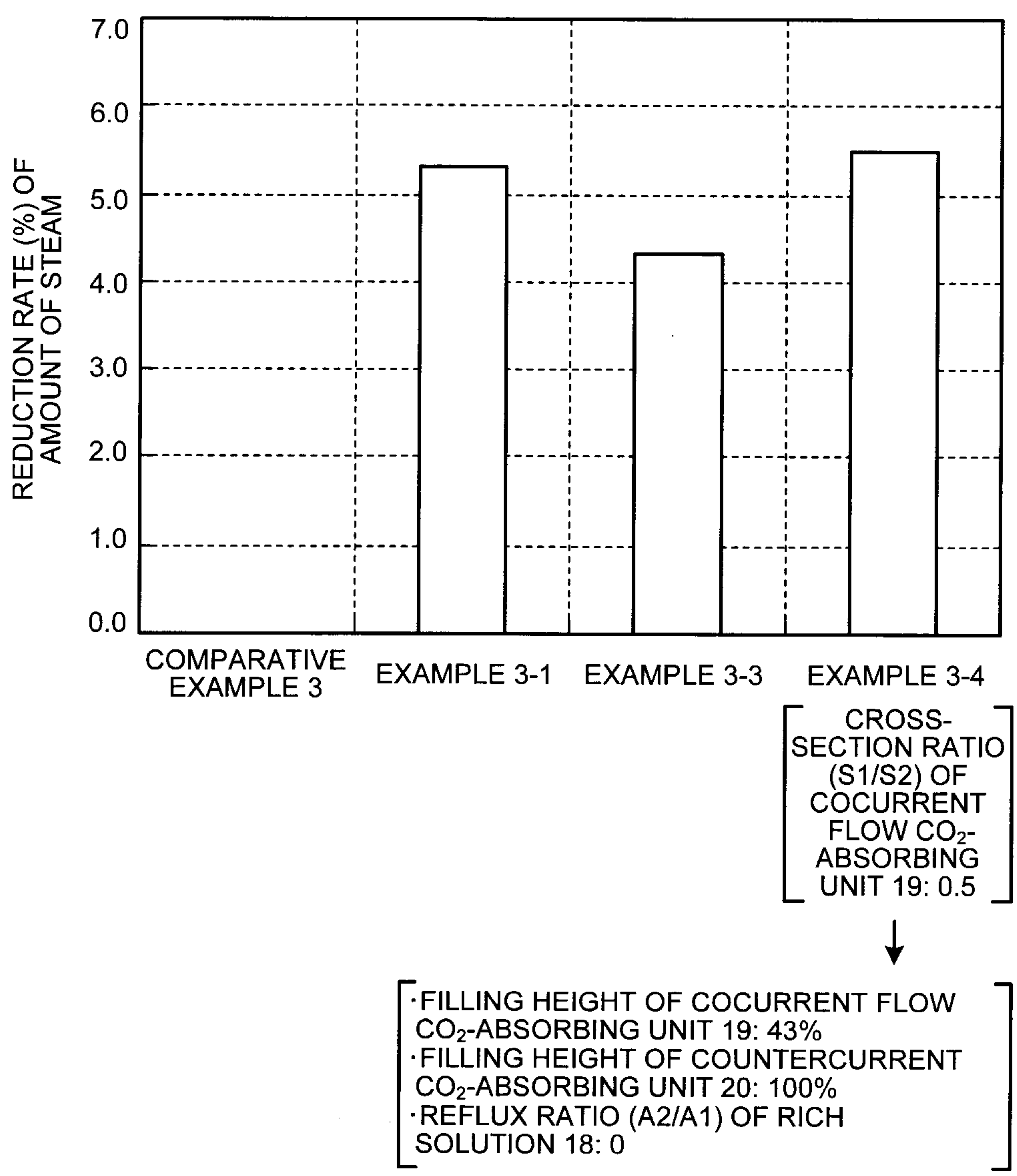

7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
REDUCTION RATE (%) OF AMOUNT OF STEAM
COMPARATIVE EXAMPLE 3
EXAMPLE 3-1
EXAMPLE 3-3
EXAMPLE 3-4
CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 0.5
·FILLING HEIGHT OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 43%
·FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20: 100%
·REFLUX RATIO (A2/A1) OF RICH SOLUTION 18: 0

FIG.8

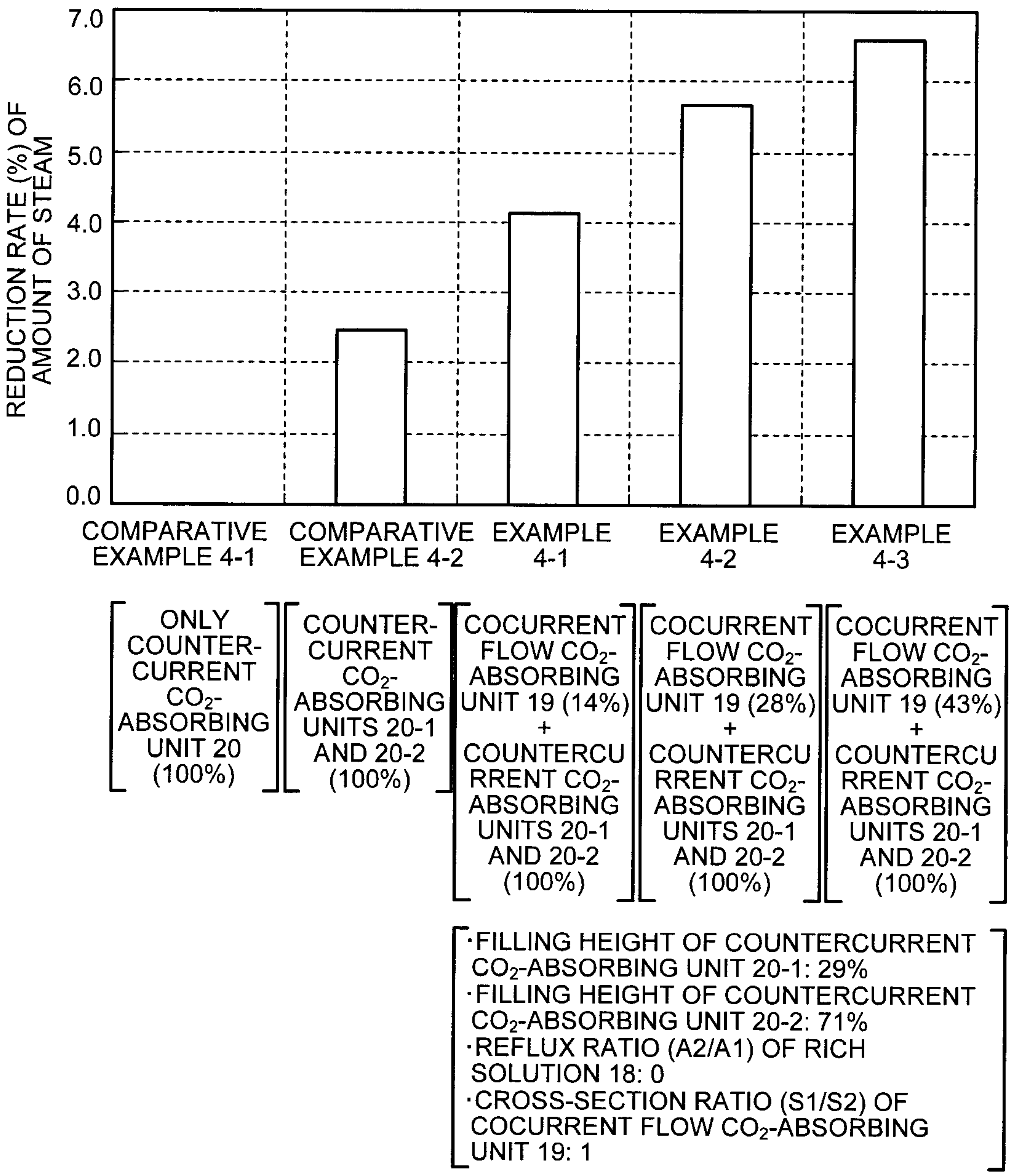
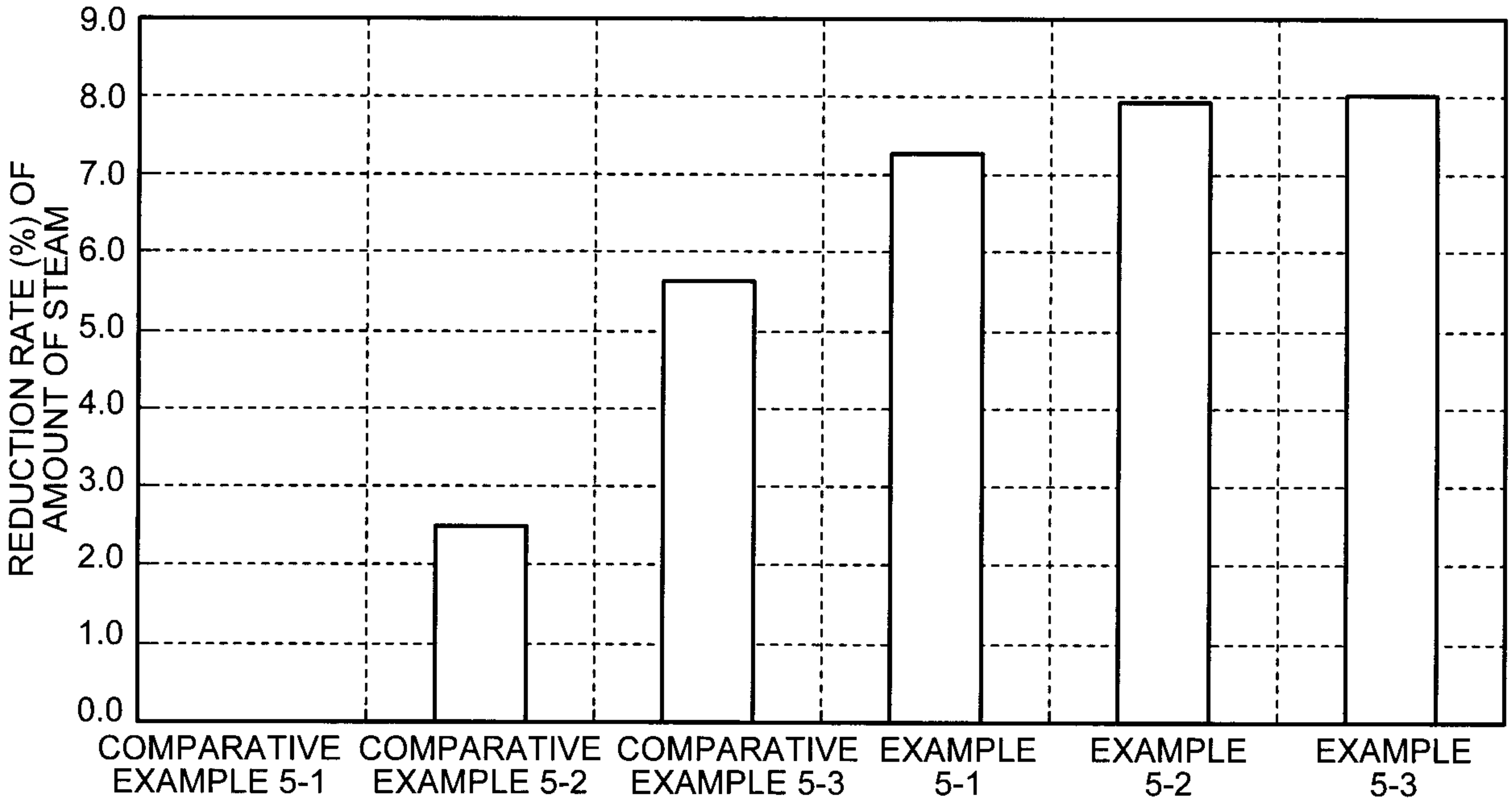

REDUCTION RATE (%) OF AMOUNT OF STEAM
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
COMPARATIVE EXAMPLE 4-1
COMPARATIVE EXAMPLE 4-2
EXAMPLE 4-1
EXAMPLE 4-2
EXAMPLE 4-3
ONLY COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)
COUNTER-CURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)
COCURRENT FLOW CO_2-ABSORBING UNIT 19 (14%) + COUNTERCURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)
COCURRENT FLOW CO_2-ABSORBING UNIT 19 (28%) + COUNTERCURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)
COCURRENT FLOW CO_2-ABSORBING UNIT 19 (43%) + COUNTERCURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)
·FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20-1: 29%
·FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20-2: 71%
·REFLUX RATIO (A2/A1) OF RICH SOLUTION 18: 0
·CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 1

FIG.9



ONLY COUNTER-CURRENT CO_2-ABSORBING UNIT 20 (100%)

COUNTERCURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)

COCURRENT FLOW CO_2-ABSORBING UNIT 19 (14%) + COUNTER-CURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)

COUNTER-CURRENT CO_2-ABSORBING UNIT 81 (14%) | COUNTER-CURRENT CO_2-ABSORBING UNIT 81 (28%) | COUNTER-CURRENT CO_2-ABSORBING UNIT 81 (43%)
+ COCURRENT FLOW CO_2-ABSORBING UNIT 19 (28%)
+ COUNTERCURRENT CO_2-ABSORBING UNITS 20-1 AND 20-2 (100%)

- FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20-1: 29%
- FILLING HEIGHT OF COUNTERCURRENT CO_2-ABSORBING UNIT 20-2: 71%
- REFLUX RATIO (A2/A1) OF RICH SOLUTION 18A: 0
- CROSS-SECTION RATIO (S1/S2) OF COCURRENT FLOW CO_2-ABSORBING UNIT 19: 1
- REFLUX RATIO (A4/A3) OF RICH SOLUTION 18B: 0


10
23
45
48
53
49
44
50
47
52
51
22
17
64
16
29
14B
12
43
65
11
15
19
20
26
31
27
33
14A
28
34
63
39
13
18
21
71
72
74
75
73
76
77
61
36
62
24
14C
41
32
37
38
17