Description

Title of Invention

HYDROGEN AND AMMONIA PRODUCTION SYSTEM

Technical Field

[0001]

The present invention relates to a system for producing hydrogen and ammonia using a wastewater from a combustion plant including a combustion chamber and a boiler.

Background Art

[0002]

In the related art, to remove ammonia contained in a wastewater from a combustion plant, a method by ion exchange and a method by stripping are known.

Patent Document 1 describes a method in which boiler blowdown water is passed through a cation exchanger to cause the cation exchanger to capture ammonia, and the cation exchanger is subjected to a regeneration treatment to obtain an ammonia concentrated wastewater. In the regeneration treatment of the cation exchanger, chemicals such as hydrochloric acid, sulfuric acid, and sodium hydroxide are added. It is also described that the ammonia concentrated wastewater is introduced into an ammonia recovery device, and ammonia is transferred to a gas phase by stripping and recovered as an ammonia gas.

[0003]

Patent Document 2 describes a technique in which, in stripping of an ammonia-containing wastewater containing hardness components (wastewater from a flue gas desulfurizer), the hardness components are removed before the ammonia-containing wastewater is introduced into a stripping device (ammonia stripping tower). First, an alkali is added to the ammonia-containing wastewater to adjust the pH (hydrogen ion exponent) to 8 to 14. Subsequently, a flocculation aid is added and the hardness components deposited as precipitates are removed. A supernatant wastewater containing no precipitate is adjusted in pH by adding an acid and supplied to the stripping device to recover an ammonia gas by stripping.

Prior Art Reference

Patent Literature

[0004]

Patent Document 1: JP 2019-098206 A
Patent Document 2: JP 2007-175673 A

Summary of Invention

Technical Problem

[0005]

In the technique of Patent Document 1, the regeneration treatment of the cation exchanger is required, that is, a large amount of chemicals for taking out ammonia captured by the cation exchanger is required, and thus the cost for obtaining an ammonia concentrated wastewater is high. Also in the technique of Patent Document 2, a large amount of chemicals for adjusting the pH is required, and thus the problem of chemicals cost cannot be solved.

In addition, when a treatment is performed after mixing both, the components of scale of a water from exhaust gas treatment increase and the ammonia concentration of boiler blowdown water decreases, and thus, it is necessary to add a large amount of a chemical agent for a pretreatment. Therefore, in the existing techniques, valuable materials contained in a wastewater from a plant cannot be efficiently recovered.

[0006]

The present invention has been made in view of the above-described problems, and an object of the present invention is to provide a hydrogen and ammonia production system that can efficiently and inexpensively produce valuable materials from a wastewater from a plant.

Solution to Problem

[0007]

A hydrogen and ammonia production system according to the present invention is a hydrogen and ammonia production system for use at a plant including a boiler that generates steam by heat of a combustion furnace or a combustion chamber and discharges boiler blowdown water and an exhaust gas treatment device that treats an exhaust gas generated from the combustion furnace or the combustion chamber and discharges a wastewater from exhaust gas treatment. The hydrogen and ammonia production system includes: a first ammonia recovery device that recovers ammonia by subjecting the wastewater from exhaust gas treatment to a stripping treatment and produces a first concentrated ammonia solution; a second ammonia recovery device that recovers ammonia by subjecting the first concentrated ammonia solution together with the boiler blowdown water to a stripping treatment and produces

a second concentrated ammonia solution; an ion removal device that causes the boiler blowdown water discharged from the second ammonia recovery device to pass therethrough such that the boiler blowdown water is separated into permeated water and a concentrated ionic solution containing residual alkaline components; a water electrolysis device that produces hydrogen by electrolyzing the permeated water; and an organic or inorganic wastewater treatment device of the plant that feeds the concentrated ionic solution as an alkali source.

Advantageous Effects of Invention

[0008]

According to the hydrogen and ammonia production system of the present invention, the first concentrated ammonia solution can be recovered by subjecting the wastewater from exhaust gas treatment, which is an ammonia-containing wastewater, to a stripping treatment, and the second concentrated ammonia solution can be recovered from the boiler blowdown water by subjecting the first concentrated ammonia solution together with the boiler blowdown water, which is an ammonia-containing wastewater, to a stripping treatment. As compared with the case where these wastewaters are separately treated to recover ammonia or these wastewaters are mixed and treated, the amounts of required chemicals can be reduced and thus the costs can be reduced. In addition, it is possible to produce hydrogen through water electrolysis of the permeated water that is obtained by using the ion removal device from the boiler blowdown water remaining after the recovery of the second concentrated ammonia solution. Therefore, the hydrogen and ammonia production system of the present invention can efficiently and inexpensively produce valuable materials from an ammonia-containing wastewater from a plant.

Brief Description of Drawings

[0009]

FIG. 1 is a block diagram illustrating an example of the present invention.

FIG. 2 is a block diagram illustrating a first modification example according to the present invention.

FIG. 3 is a block diagram illustrating a second modification example according to the present invention.

FIG. 4 is a block diagram illustrating a third modification example according to the present invention.

Description of Embodiments

[0010]

A hydrogen and ammonia production system of the present invention will be described below with reference to FIGS. 1 to 4. In the present invention, unless it is necessary to distinguish between ionic and molecular forms, the denotation of "ammonia" includes both ammonia molecules and ammonia ions. Thus, an "ammonia-containing wastewater" also includes a wastewater containing ammonia in the form of ammonia ion.

In the drawings, a reference sign consisting of only numeric character(s) represents a physical element such as a device, a part, and a portion related to the present system in the examples and modification examples of the present invention. A reference sign consisting of a combination of the letter F and numeric character(s) represents a fluid such as a liquid or a gas generated in the present system, and a reference sign consisting of a combination of the letter P and numeric character(s) represents a position. Note that the examples and the modification examples described below are merely illustrative, and there is no intention to exclude various modifications and applications of techniques that are not explicitly described. Each configuration described below can be variously modified and implemented without deviating from the gist thereof. In addition, each configuration described below can be selected as appropriate except for a configuration essential to the present invention or can be combined with a known configuration.

[0011]

1. Examples

A. Configuration

FIG. 1 is a block diagram illustrating a hydrogen and ammonia production system 1 according to an example. A hydrogen and ammonia production system 1 includes a plant 10, a valuable material generation facility 20, and a general wastewater treatment device 40. The plant 10 includes at least: a boiler 16 that generates steam by heat of a combustion chamber (or a combustion furnace) 11; and an exhaust gas treatment device 19 that treats an exhaust gas of the combustion chamber 11 and discharges a wastewater F1 from exhaust gas treatment. The valuable material generation facility 20 includes at least; a first ammonia recovery device 21 that recovers ammonia contained in the wastewater F1 from exhaust gas treatment of the plant 10 by

subjecting the wastewater F1 from exhaust gas treatment to a stripping treatment and produces a first concentrated ammonia solution F4; a second ammonia recovery device 22 that produces a second concentrated ammonia solution F8 by subjecting a boiler blowdown water F3 of the plant 10 together with the first concentrated ammonia solution F4 to a stripping treatment; an ion removal device 27 that removes alkaline components remaining in a wastewater F9 of the second ammonia recovery device 22 from the wastewater F9; a water electrolysis device 28 that produces hydrogen F12 through water electrolysis of permeated water F11 obtained by removal of the alkaline components. The general wastewater treatment device 40 includes an organic or inorganic wastewater treatment device that treats a plant wastewater F16 discharged from the plant 10 by using a concentrated ionic solution F10, which is the alkaline components removed by the ion removal device 27, as an alkali source until the plant wastewater F16 becomes dischargeable.

As the plant 10, a plant including a combustion chamber and a boiler that generates steam by heat of the combustion chamber, that is, a combustion plant can be applied, and the plant 10 can be applied to, for example, various plants such as a waste incineration plant, a thermal power plant, and a chemical plant. However, in a plant to which the hydrogen and ammonia production system 1 is applied, all the components in FIG. 1 do not need to be arranged in the same site, and a plurality of components in FIG. 1 may be arranged separately in different sites. In that case, the hydrogen and ammonia production system 1 may be configured to be appropriately connected by a pipeline or a transportation route for an automobile or the like. The valuable material generation facility 20 and the general wastewater treatment device 40 may be disposed in the same site as the plant 10 as incidental facilities of the plant 10, or may be disposed in sites different from each other and appropriately connected to each other by a pipeline or a transportation route for an automobile or the like so as to constitute the hydrogen and ammonia production system 1.

[0012]

Each configuration in FIG. 1 and the effects thereof will be described.

In the plant 10, the combustion chamber 11 (or a combustion furnace) is a facility in which fuel is burned. When the plant 10 is, for example, a waste incineration plant, the fuel is typically a waste (municipal waste or industrial waste). When the plant 10 is a thermal power plant or a chemical plant, the fuel is typically coal, petroleum, natural gas, woody biomass, green fuel such as biogas produced by fermentation, or the like. As the fuel in the combustion

chamber 11, ammonia or hydrogen, for example, ammonia or hydrogen produced by the hydrogen and ammonia production system 1 may be used. The combustion chamber 11 may be provided as equipment attached to the boiler 16 (for example, built in the boiler 16) to be described below.

[0013]

An exhaust gas generated in the combustion chamber 11 sequentially flows through a flue gas duct as follows, and is discharged into the atmosphere from a stack 15. That is, the exhaust gas flows through an exhaust gas treatment device 19 including at least a dust collecting device 13 that removes dusts from the exhaust gas and a wet-type treatment device 14 that removes harmful components such as sulfur oxides (SOx) from the exhaust gas from which the dusts have been removed by the dust collecting device 13 using a method such as a lime-gypsum method, and through the stack 15 that discharges the exhaust gas from which the harmful components have been removed to the atmosphere in this order. Here, to reduce nitrogen oxides (NOx), a chemical agent (denitration agent) containing ammonia or ammonia nitrogen as a reducing agent for the nitrogen oxides is supplied from an ammonia supply device 12 to between the combustion chamber 11 and the wet-type treatment device 14. A wastewater F1 from exhaust gas treatment which is an ammonia-containing wastewater is discharged from the wet-type treatment device 14. The wastewater F1 from exhaust gas treatment contains components of scale such as Ca^{2+} and Mg^{2+}. The ammonia concentration of the wastewater F1 from exhaust gas treatment is about 50 to 50000 mg/L, preferably about 1000 to 20000 mg/L, and more preferably about 2000 to 10000 mg/L. The wastewater F1 from exhaust gas treatment discharged is introduced into the first ammonia recovery device 21 of the valuable material generation facility 20 to be described below. The wastewater F1 from exhaust gas treatment may be stored in a wastewater storage tank (not illustrated) and thereafter introduced into the first ammonia recovery device 21.

[0014]

The boiler 16 is a device that recovers heat of the combustion chamber 11 and generates steam F2. The boiler 16 includes: a pure water production device 50 that produces pure water from tap water or industrial water; an additive supply device 51 that adds an additive such as a pH adjuster to the pure water produced; a steam drum 52 that stores the pure water (boiler water) to which the additive is added; a heat recovery device 53 such as a heat transfer tube or a superheater tube that converts the boiler water stored in the steam drum 52 into the steam F2 by using heat of an exhaust gas; a steam turbine 54

that rotates an impeller by the steam produced by the heat recovery device 53 and stored in the steam drum 52; a generator 55 that generates power by a rotational force of the impeller of the steam turbine 54; a condenser 56 that returns the steam (waste steam) having rotated the impeller of the steam turbine 54 to water; and a deaerator 57 that removes a dissolved gas from condensate produced by the condenser 56 and supplies the condensate to the steam drum 52.

Examples of the type of the chemical added here include a cleaning agent, an anticorrosive (deoxidating agent), and a scale inhibitor that contains at least ammonia for preventing corrosion.

The boiler 16 has a mechanism for discharging (blowing) some of the boiler water to the outside via a blowdown piping to prevent concentration of various components contained in the boiler water. The boiler water discharged to the outside of the boiler 16 is referred to as the boiler blowdown water F3. The boiler blowdown water F3 is a wastewater (ammonia-containing wastewater) containing ammonia supplied by the additive, and is introduced into a second ammonia recovery device 22 of the valuable material generation facility 20 to be described below. In consideration of corrosion resistance, the boiler blowdown water F3 has a pH value of about 9 to 10 so as to adjust the pH value of the water stored in the steam drum 52 to about 9 to 10 (for example, a pH value of about 10.3). The boiler blowdown water F3 may be stored in a wastewater storage tank (not illustrated) and thereafter introduced into the second ammonia recovery device 22.

The electric power generated by the generator 55 is used as electric power in the hydrogen and ammonia production system 1, and surplus electric power can be sold to a power company. The steam F2 can also be used for heat utilization equipment inside and outside the hydrogen and ammonia production system 1.

[0015]

The valuable material generation facility 20 produces valuable materials using a wastewater (ammonia-containing wastewater) discharged from the plant 10. Specific examples of the valuable materials produced in the valuable material generation facility 20 include hydrogen and ammonia, and urea and methane are also produced.

[0016]

In the valuable material generation facility 20 illustrated in FIG. 1, the first ammonia recovery device 21 is a device that recovers ammonia contained in the wastewater F1 from exhaust gas treatment through a stripping treatment

and produces a first concentrated ammonia solution F4. A first pH adjuster supply device 23 is a device that supplies an alkaline agent (for example, sodium hydroxide) for adjusting the pH inside the first ammonia recovery device 21. In the first ammonia recovery device 21, for example, a diffusion tower (stripping tower) partitioned into multiple sections by a filler, a tray, or a separation cylinder is provided, and the stripping tower includes one stripping tower that is long in the vertical direction or a plurality of stripping towers continuously connected in series. In the first ammonia recovery device 21 of FIG. 1, one stripping tower is used as an example, and the stripping tower is divided into three sections in the vertical direction by two trays as an example. One stripping tower may be divided into four or more sections by three or more trays or the like.

[0017]

In the first ammonia recovery device 21, the wastewater F1 from exhaust gas treatment having a high temperature (about 70°C to about 90°C) is injected from an upper portion of the stripping tower. The wastewater F1 from exhaust gas treatment gradually descends down in the stripping tower while being diffused in a mist form. On the other hand, high-temperature steam is supplied from a lower portion of the stripping tower so as to oppose the wastewater F1 from exhaust gas treatment descending down. This steam moves upward in the stripping tower while being diffused in a mist form. By such gas-liquid contact between the wastewater F1 from exhaust gas treatment and the steam, ammonia in the wastewater F1 from exhaust gas treatment is transferred to a gas phase and recovered.

Here, the pH value of the wastewater from exhaust gas treatment in the first ammonia recovery device is preferably greater than 8 and smaller than 9.5. When the pH value is smaller than 8, it is difficult to diffuse ammonia.

Further, the dissolved amounts of Ca^{2+} and Mg^{2+} which are the components of scale in the wastewater F1 from exhaust gas treatment depend on the pH-value, and when the pH value exceeds 9.5, the components of scale are more likely to be deposited. Since the wastewater F1 from exhaust gas treatment contains a large amount of components of scale, the pH value is not increased in the first ammonia recovery device 21, and the stripping is performed in a pH value range in which scales are unlikely to be deposited.

That is, the wastewater F1 from exhaust gas treatment has a relatively high ammonia concentration, and it is not necessary to excessively increase the pH value in the stripping for recovering a required amount of ammonia as an ammonia source to be mixed with the boiler blowdown water F3 as described

below. In addition, since ammonia is likely to be liberated from the wastewater F1 from exhaust gas treatment at a high temperature (about 70°C to about 90°C), it is not necessary to increase the pH value up to a range in which scales are likely to be generated. Accordingly, the amount of the alkaline agent fed from the first pH adjuster supply device 23 can be reduced, and thus the chemicals cost can be reduced.

[0018]

The ammonia having been transferred into a gas phase and the steam are discharged from the upper portion of the stripping tower and recovered as the first concentrated ammonia solution F4, and then introduced into the second ammonia recovery device 22 together with the boiler blowdown water F3. The ammonia concentration of the first concentrated ammonia solution F4 is, for example, about several % to 10%. As the steam supplied from the lower portion of the stripping tower, the steam F2 generated by the boiler 16 may be used, or another steam may be used. Further, when a waste steam that is the steam F2 after being supplied to the steam turbine 54 is reused, the cost for utilizing steam can be reduced.

[0019]

The second ammonia recovery device 22 is a device that recovers ammonia contained in the boiler blowdown water F3 by a stripping treatment and produces a second concentrated ammonia solution F8. A second pH adjuster supply device 24 is a device that supplies an alkaline agent (for example, sodium hydroxide or the like) for adjusting the pH inside the second ammonia recovery device 22. The second ammonia recovery device 22 is also provided with a diffusion tower (stripping tower) similar to that of the first ammonia recovery device 21.

[0020]

In the second ammonia recovery device 22, the first concentrated ammonia solution F4 and the boiler blowdown water F3 having a high temperature (about 70°C to about 90°C) are injected from an upper portion of the stripping tower. In the present example, a mixed liquid in which the first concentrated ammonia solution F4 and the boiler blowdown water F3 are mixed in advance is injected. The mixed liquid of the boiler blowdown water F3 and the first concentrated ammonia solution F4 gradually descends down in the stripping tower while being diffused in a mist form. On the other hand, high-temperature steam is supplied from a lower portion of the stripping tower so as to oppose the mixed liquid descending down. This steam moves upward in the stripping tower while being diffused in a mist form. By such gas-liquid contact

between the mixed liquid and the steam, ammonia in the mixed liquid is transferred to a gas phase and recovered. By feeding the first concentrated ammonia solution F4 containing a high concentration of ammonia together with the boiler blowdown water F3 containing a relatively low concentration of ammonia into the second ammonia recovery device 22, the ammonia concentration in the boiler blowdown water F3 can be increased.

In addition, since the boiler blowdown water F3 and the first concentrated ammonia solution F4 contain less components of scale, the pH values thereof can be increased without concern for scale deposition. Here, the pH value of the mixed liquid can be adjusted to, for example, 10 to 12 by feeding an alkaline agent from the second pH adjuster supply device 24. At this time, both the boiler blowdown water F3 and the first concentrated ammonia solution have a high pH value, and thus the amount of the alkaline agent supplied from the second pH adjuster supply device 24 can be small.

Further, since the boiler blowdown water F3 has a high temperature (about 70°C to about 90°C) and the first concentrated ammonia solution F4 also has a high temperature, the cost for heating each liquid can be reduced.

In this way, in the second ammonia recovery device 22, the efficiency of recovering ammonia by stripping can be increased.

Note that the first concentrated ammonia solution F4 and the boiler blowdown water F3 may be separately injected into the second ammonia recovery device 22 without being mixed in advance, and may be mixed in the second ammonia recovery device 22.

[0021]

The ammonia having been transferred into a gas phase and the steam are discharged from the upper portion of the stripping tower and recovered as the second concentrated ammonia solution F8. The ammonia concentration of the second concentrated ammonia solution F8 is higher than that of the first concentrated ammonia solution F4, and ranges from about 25% to about 50%, for example. The second concentrated ammonia solution F8 can be supplied, for example, as a fuel or a feedstock to ammonia utilization equipment 41 such as a chemical plant or an ammonia gas turbine. Alternatively, the second concentrated ammonia solution F8 may be supplied from the ammonia supply device 12 into an exhaust gas for use as a denitration agent (a reducing agent for reducing NOx to nitrogen) or may be used for manufacturing chemical products. As the steam supplied from the lower portion of the stripping tower, the steam F2 generated by the boiler 16 may be used, or another steam may be

used. Further, when a waste steam that is the steam F2 after being supplied to the steam turbine 54 is reused, the cost for utilizing steam can be reduced.

[0022]

A wastewater F5 from which ammonia has been removed is accumulated at the lower portion of the stripping tower of the first ammonia recovery device 21. The wastewater F5 is introduced into a flocculation treatment tank 26.

The flocculation treatment tank 26 is a tank for removing a component F7 (for example, Ca^{2+}, Mg^{2+}, or the like) of scale contained in the wastewater F5. The flocculation treatment tank 26 is provided with a flocculant supply device 25 that supplies a flocculant for flocculating the component F7 of scale in the wastewater F5. As the flocculant supplied by the flocculant supply device 25, an inorganic flocculant (for example, a ferric chloride solution) may be used or an organic flocculant (for example, a polymer flocculant) may be used. The component F7 of scale in the wastewater F5 is deposited as solids in the flocculation treatment tank 26, and thus can be easily removed. A wastewater F6 (supernatant solution) from flocculation obtained by removing the component F7 of scale from the wastewater F5 is supplied to the general wastewater treatment device 40. The wastewater F5 may be directly supplied to the general wastewater treatment device 40 without installing the flocculation treatment tank 26.

[0023]

A wastewater F9 from which ammonia has been mostly removed is accumulated at the lower portion of the stripping tower of the second ammonia recovery device 22. The wastewater F9 is introduced into the ion removal device 27.

The ion removal device 27 is a device that removes alkaline components (unnecessary ions) such as ammonia and sodium hydroxide remaining in the wastewater F9 after the stripping treatment. The ion removal device 27 is provided with an ion-exchange tower filled with, for example, an RO membrane (reverse osmotic membrane) or an ion-exchange resin (for example, a high-temperature ion exchange resin). The RO membrane is a membrane that allows hydrogen ions (H^+) and hydroxide ions (OH^-) in water to pass therethrough and prevents other ions (for example, Ca^{2+}, Mg^{2+}, and NH_4^+) from passing therethrough. The ion-exchange resin is gel-like synthetic resin beads for substituting unnecessary ions in water with hydrogen ions or hydroxide ions, and for example, a heat-resistant cation exchange resin is used. By these actions, the wastewater F9 is separated into the permeated water F11 from which the unnecessary ions have been removed and the concentrated ionic

solution F10 containing the unnecessary ions. The permeated water F11 generated here is supplied to the water electrolysis device 28. The concentrated ionic solution F10 containing ammonia components and other residual alkaline components is supplied to the general wastewater treatment device 40 and reused as an alkali source (ammonia source) in an organic or an inorganic wastewater treatment.

As a result, the residual alkaline components contained in the concentrated ionic solution F10 can be utilized as an ammonia source for wastewater treatment. In other words, the wastewater F9 of the second ammonia recovery device 22 can be effectively reused as a resource. In addition, the wastewater F9 is a wastewater after ammonia is recovered by the second ammonia recovery device, and the amount of chemicals for recovering ammonia can be small.

[0024]

The water electrolysis device 28 is a device that produces the hydrogen F12 by electrolyzing the permeated water F11 generated by the ion removal device 27. In general, water containing no impurities or very little impurities, that is, pure water or water substantially equivalent to pure water is supplied to the water electrolysis device to be electrolyzed. Thus, the permeated water F11 is pure water or water substantially equivalent to pure water. The hydrogen F12 produced here is supplied as a fuel or a feedstock to hydrogen utilization equipment 42 such as a chemical plant, a fuel cell, and a hydrogen gas turbine, for example. Oxygen that can be generated during electrolysis of the permeated water F11 may be released to the atmosphere, may be supplied into the combustion chamber 11 as a combustion accelerator, or may be stored in an oxygen storage tank (not illustrated).

In general, a water electrolysis device includes a heating device for heating pure water or the like having a room temperature to efficiently perform electrolysis, and energy for heating pure water having a room temperature is very large. However, the water electrolysis device 28 according to the example can reduce the energy required for the heating device. This is because the temperature of the boiler blowdown water F3, which is a feedstock for the water electrolysis device 28, is high, and the temperature of the permeated water F11 separated by the ion removal device 27 is also high, that is, they are more easily adjusted to a high temperature than when they have a room temperature.

[0025]

The general wastewater treatment device 40 is a facility for wastewater treatment and includes various devices such as an organic treatment device and an inorganic treatment device for treating the plant wastewater F16 including various wastewaters discharged from a plant. The organic treatment device is a wastewater treatment device that is provided with a nitrification tank, a denitrification tank, an aeration tank, and the like and performs a biological treatment (wastewater treatment by the action of microorganisms). The inorganic treatment device is a wastewater treatment device that performs inorganic water treatment. In the organic treatment device, for example, a nitrification tank, a denitrification tank, an aeration tank, and the like are provided, and ammonia in a wastewater is converted into nitrogen and removed by the action of nitrification bacteria, denitrification bacteria, and the like. In the inorganic treatment device, for example, a chemical reaction tank, a precipitation tank, a filtration tank, and the like are provided, and impurities, metals, and the like in a wastewater are chemically removed. The wastewater having been treated by the general wastewater treatment device 40 may be reused in the plant 10, the valuable material generation facility 20, and the general wastewater treatment device 40, or may be discharged to the outside.

[0026]

B. Operational Effects

In general, the ammonia concentration suitable for a stripping treatment is about 2000 mg/L. However, the ammonia concentration of the boiler blowdown water F3 is relatively low and thus is often unsuitable for a stripping treatment. For example, it is assumed that the water temperature of the boiler blowdown water F3 is about 80°C, the discharge amount is about 150 m^3/day, and the ammonia concentration is about 600 mg/L, while the water temperature of the wastewater F1 from exhaust gas treatment is about 80°C, the discharge amount is about 80 m^3/day, and the ammonia concentration is 3000 mg/L. In this case, since the discharge amount of the boiler blowdown water F3 is large and the concentration of the ammonia contained in the boiler blowdown water F3 is low, it is difficult to efficiently recover ammonia when the stripping treatment is performed by using only the boiler blowdown water F3.

[0027]

On the other hand, in the hydrogen and ammonia production system 1 described above, the wastewater F1 from exhaust gas treatment is first subjected to a stripping treatment in the first ammonia recovery device 21 to recover ammonia. At this time, even when the pH value of the wastewater F1 from exhaust gas treatment is about 9, free ammonia accounts for about 90% at

a high temperature of about 80°C. Further, when the free ammonia is fully recovered, about 4 m^3 of the first concentrated ammonia solution F4 having an ammonia concentration of about 54000 mg/L can be recovered. The first concentrated ammonia solution F4 recovered and the boiler blowdown water F3 are introduced into the second ammonia recovery device 22 and subjected to a stripping treatment again.

[0028]

Here, the ammonia concentration of the mixed liquid of the boiler blowdown water F3 and the first concentrated ammonia solution F4 is about 2000 mg/L, that is, an ammonia concentration suitable for a stripping treatment is obtained. Thus, the efficiency of stripping ammonia in the second ammonia recovery device 22 is improved. Further, when the pH value of the mixed liquid is adjusted and then the stripping treatment is performed in the second ammonia recovery device 22, for example, an ammonia solution having an ammonia concentration of 25%, which is equivalent to those distributed in the market, can be easily obtained as the second concentrated ammonia solution F8.

[0029]

At this time, the concentration of the ammonia remaining in the wastewater F9 discharged from the second ammonia recovery device 22 is about 200 mg/L. When the wastewater F9 is supplied to the ion removal device 27 and concentrated by using a high-temperature ion-exchange resin, the concentrated ionic solution F10 containing concentrated residual alkaline components and the permeated water F11 can be obtained. The volume of the concentrated ionic solution F10 obtained here is about 6 m^3, and the concentration of the residual alkaline components is about 5000 mg/L. When the concentration of the residual alkaline components is converted to ammonia nitrogen, the ammonia nitrogen can be used as an alkali source (ammonia source) for treating an organic wastewater up to about 200 m^3 per day, which is suitable for maintaining bacteria in an organic biological treatment.

[0030]

In the hydrogen and ammonia production system 1 described above, the first concentrated ammonia solution F4 is produced from the wastewater F1 from exhaust gas treatment in the first ammonia recovery device 21, and the second concentrated ammonia solution F8 is produced by feeding the first concentrated ammonia solution F4 together with the boiler blowdown water F3 into the second ammonia recovery device 22, whereby ammonia can be recovered more efficiently than when the wastewater F1 from exhaust gas

treatment and the boiler blowdown water F3 are separately subjected to the stripping treatment or when the wastewater F1 from exhaust gas treatment and the boiler blowdown water F3 are mixed and then subjected to the stripping treatment. Further, unlike the techniques of Patent Documents 1 and 2, it is not necessary to capture ammonia contained in the boiler blowdown water F3 through pretreatment using a large amount of chemicals or adjust the pH value of the wastewater F1 from exhaust gas treatment to remove components of scale and then adjust the pH value again by using a large amount of chemicals, and thus ammonia can be easily recovered. Therefore, according to the hydrogen and ammonia production system 1 described above, the wastewater of the plant 10 can be reused for producing valuable materials (for example, hydrogen and ammonia) and chemical products, and valuable materials can be efficiently and inexpensively produced from the wastewater of the plant 10.

[0031]

2. First Modification Example

FIG. 2 is a block diagram illustrating a configuration of a hydrogen and ammonia production system 1′ according to a first modification example. The same components as those described in the example are denoted by the same reference signs, and descriptions of such components and effects thereof will be omitted. The hydrogen and ammonia production system 1′ includes a valuable material generation facility 20′ including a second flow path that supplies some of the first concentrated ammonia solution F4 to the second ammonia recovery device 22 at a position different from a position at which the boiler blowdown water F3 is supplied. In the valuable material generation facility 20′, the first concentrated ammonia solution F4 is caused to flow through the second flow path when a ratio of the ammonia amount of the boiler blowdown water F3 and the ammonia amount of the first concentrated ammonia solution F4 in a first flow path is a certain value or greater.

[0032]

The valuable material generation facility 20′ includes: a first flow path 60 that mixes the first concentrated ammonia solution F4 with the boiler blowdown water F3; a second flow path 61 that is branched from the first flow path 60 and supplies the first concentrated ammonia solution F4 to the second ammonia recovery device 22; a control valve 62 that adjusts the flow rate of the first concentrated ammonia solution F4 flowing into the second flow path 61; a control device 63 that controls the control valve 62; an ammonia concentration meter 64 that measures the ammonia concentration of the boiler blowdown water F3; a flow meter 65 that measures the flow rate of the boiler blowdown

water F3; an ammonia concentration meter 66 that measures the ammonia concentration of the first concentrated ammonia solution F4 in the first flow path 60; and a flow meter 67 that measures the flow rate of the first concentrated ammonia solution F4 in the first flow path 60.

The control device 63 calculates a ratio of the ammonia amount of the first concentrated ammonia solution F4 to the ammonia amount of the boiler blowdown water F3 based on values of ammonia concentrations and flow rates measured by the ammonia concentration meters and the flow meters for the respective liquids. When the ratio of the ammonia amounts is a predetermined value, for example, 2 or greater, the control device 63 determines that a sufficient amount of ammonia is supplied to the boiler blowdown water F3, and opens the control valve 62 to supply, to the second flow path 61, a predetermined amount of the first concentrated ammonia solution F4, for example, about 1/10 of the amount in the first flow path, such that the ratio of the ammonia amounts does not fall below the predetermined value. Alternatively, for example, pH meters may be installed in substitution for the ammonia concentration meters, and the ammonia concentrations may be obtained based on measured pH values.

Further, when a position of the second ammonia recovery device 22 in the vertical direction at which the mixed liquid of the boiler blowdown water F3 mixed with the first concentrated ammonia solution F4 is supplied is defined as a third position P3, and a position in the vertical direction at which the first concentrated ammonia solution F4 having flowed through the second flow path 61 is supplied to the second ammonia recovery device 22 is defined as a fourth position P4, the fourth position P4 is preferably set at a position different from the third position P3, and more preferably the fourth position P4 is set at a position above the third position P3.

In FIG. 2, in the second ammonia recovery device 22 whose interior is partitioned into three sections, the fourth position P4 is arranged in a section above the third position P3.

In addition, the first concentrated ammonia solution F4 in the first flow path may be supplied to a position at which the first concentrated ammonia solution F4 is mixed with the boiler blowdown water F3 in the second ammonia recovery device 22 without being mixed with the boiler blowdown water F3 in advance, and, for example, may be supplied at the vicinity of the third position P3 and then mixed with the boiler blowdown water F3.

[0033]

By setting the third position P3 and the fourth position P4 to be different from each other, the liquid to be treated supplied from each position in a mist form can be easily diffused uniformly in the stripping tower, and the vaporization efficiency of ammonia can be improved. Further, by setting the fourth position P4 above the third position P3, the time and distance required for vaporizing ammonia from the first concentrated ammonia solution F4 supplied to the second ammonia recovery device 22 can be easily secured, and the vaporization efficiency of ammonia can be further improved. Therefore, the concentration of ammonia in the second ammonia recovery device 22 can be promoted.

[0034]

3. Second Modification Example

FIG. 3 is a block diagram illustrating a configuration of a hydrogen and ammonia production system 1″ according to a second modification example. The same components as those described in the example are denoted by the same reference signs, and descriptions of such components and effects thereof will be omitted. The hydrogen and ammonia production system 1″ includes a valuable material generation facility 20″ that causes some of the first concentrated ammonia solution F4 and some of the second concentrated ammonia solution F8 to circulate in the first ammonia recovery device 21 and the second ammonia recovery device 22, respectively.

[0035]

In the valuable material generation facility 20″, some of the first concentrated ammonia solution F4 is fed into the first ammonia recovery device 21 again via a first circulation path 31. Similarly, some of the second concentrated ammonia solution F8 is fed into the second ammonia recovery device 22 again via a second circulation path 32. By circulating some of the first concentrated ammonia solution F4 and some of the second concentrated ammonia solution F8 in this way, the concentration of ammonia contained in these concentrated solutions can be further increased. In addition, it is possible to obtain the second concentrated ammonia solution F8 which is more concentrated in accordance with the change in the flow rate of the boiler blowdown water F3.

[0036]

Here, a position in the vertical direction at which the wastewater F1 from exhaust gas treatment is supplied to the first ammonia recovery device 21 is defined as a first position P1, and a position in the vertical direction at which the first concentrated ammonia solution F4 is fed again from the first

circulation path 31 is defined as a second position P2. Then, the second position P2 may be set at the same position as the first position P1, but is preferably set at a position different from the first position P1. More preferably, the second position P2 is set above the first position P1. In FIG. 2, in the first ammonia recovery device 21 whose interior is partitioned into three sections, the second position P2 is arranged in the uppermost section and the first position P1 is arranged in a section below the second position P2. Note that the same effect can be obtained even when these positions are arranged in the same section as long as they are located at different positions in the vertical direction.

[0037]

By setting the first position P1 and the second position P2 to be different from each other, the liquid to be treated supplied from each position in a mist form can be easily diffused uniformly in the stripping tower, and the vaporization efficiency of ammonia can be improved. Further, increase in the pH value of the wastewater F1 from exhaust gas treatment due to the mixing of the wastewater F1 from exhaust gas treatment and the first concentrated ammonia solution F4 can be suppressed, and the deposition of components of scale can be suppressed. Furthermore, by setting the second position P2 above the first position P1, the time and distance required for vaporizing ammonia from the first concentrated ammonia solution F4 fed again into the first ammonia recovery device 21 can be easily secured, and the vaporization efficiency of ammonia can be further improved. Therefore, the concentration of ammonia in the first ammonia recovery device 21 can be promoted.

[0038]

Similarly, a position in the vertical direction at which the second concentrated ammonia solution F8 is fed again from the second circulation path 32 is defined as a fifth position P5.

Then, the fifth position P5 may be set at the same position as the third position P3 or the fourth position P4, but is preferably set at a position different from the third position P3 and the fourth position P4. More preferably, the fifth position P5 is set above the third position P3 and the fourth position P4.

[0039]

By setting the third position P3, the fourth position P4, and the fifth position P5 to be different from each other, the liquid to be treated supplied from each position in a mist form can be easily diffused uniformly in the stripping tower, and the vaporization efficiency of ammonia can be improved. Further, by setting the fifth position P5 above the third position P3 and the

fourth position P4, the time and distance required for vaporizing ammonia from the second concentrated ammonia solution F8 fed again to the second ammonia recovery device 22 can be easily secured, and the vaporization efficiency of ammonia can be further improved. Therefore, the concentration of ammonia in the second ammonia recovery device 22 can be promoted.

Therefore, according to the hydrogen and ammonia production system 1″ described above, the wastewater of the plant 10 can be reused for producing valuable materials (for example, hydrogen and ammonia) and chemical products, and valuable materials can be efficiently and inexpensively produced from the wastewater of the plant 10.

[0040]

4. Third Modification Example

FIG. 4 is a block diagram illustrating a configuration of a hydrogen and ammonia production system 1‴ according to a third modification example. The same components as those described in the example and the first modification example are denoted by the same reference signs, and descriptions of such components and effects thereof will be omitted. The hydrogen and ammonia production system 1‴ according to the third modification example is applied to a plant 10‴ including a carbon dioxide separation device 18, and includes a valuable material generation facility 20‴ including a urea production device 33 and a methanation device 34.

[0041]

The carbon dioxide separation device 18 is a device for recovering carbon dioxide F13 contained in an exhaust gas. As a method for recovering the carbon dioxide F13, various known methods can be employed. For example, the carbon dioxide F13 may be recovered from an exhaust gas by using a polymer separation membrane (carbon dioxide separation membrane). Alternatively, the carbon dioxide F13 may be recovered by bringing an exhaust gas into contact with a medium having high absorption capacity or adsorption capacity with respect to the carbon dioxide F13. When a solid medium is used, the carbon dioxide F13 in an exhaust gas may be caused to be adsorbed on active carbon or zeolite, and the carbon dioxide F13 may be recovered by heating or depressurization. When a liquid medium is used, the carbon dioxide F13 may be caused to be absorbed in an amine solution, a calcium carbonate solution, an ammonia solution, or the like and recovered.

[0042]

The carbon dioxide F13 recovered, and the hydrogen F12 and the concentrated ammonia solution F8 produced in the hydrogen and ammonia production system 1″′ can be used for various applications.

In FIG. 3, the carbon dioxide F13 recovered and the concentrated ammonia solution F8 can be supplied to the urea production device 33, and the carbon dioxide F13 recovered and the hydrogen F12 can be supplied to the methanation device 34.

The urea production device 33 is a device that produces a urea F14 (CH_4N_2O) by synthesizing the carbon dioxide F13 and the second concentrated ammonia solution F8. The urea production device 33 is provided with a reactor (non-catalytic reactor) for maintaining a high-temperature and high-pressure state, and the urea F14 is produced in the reactor. The urea F14 produced here is supplied to urea utilization equipment 43. The urea utilization equipment 43 includes, for example, a chemical plant and a plant factory in which the urea F14 is used as a fertilizer.

[0043]

The methanation device 34 is a device that generates a methane F15 (CH_4) by synthesizing the carbon dioxide F13 and the hydrogen F12. Here, for example, the methane F15 is synthesized by a methanation reaction via a co-electrolysis reaction or a Sabatier reaction. The methanation device 34 is provided with a reactor (catalytic reactor) including therein a catalyst for methane synthesis, and the methane F15 is generated in the reactor. The methane F15 generated here is supplied to methane gas utilization equipment 44. The methane gas utilization equipment 44 includes, for example, a building and equipment (gas pipe) in which the methane F15 is used as a fuel (city gas) and a gas engine that generates electric power by burning the methane F15.

[0044]

As described above, by providing the carbon dioxide separation device 18 in the plant 10″′, the carbon dioxide F13 in an exhaust gas can be removed, and the discharge amount of the carbon dioxide F13 discharged from the stack 15 can be significantly reduced. Further, by providing the urea production device 33 in the valuable material generation facility 20″′, the urea F14 can be easily produced by using the carbon dioxide F13 described above and the second concentrated ammonia solution F8 produced in the valuable material generation facility 20″′. Furthermore, by providing the methanation device 34 in the valuable material generation facility 20″′, the methane F15 can be produced by using the carbon dioxide F13 described above and the hydrogen F12 produced in the valuable material generation facility 20″′. Therefore,

according to the hydrogen and ammonia production system 1‴, the wastewater of the plant 10‴ can be reused for producing valuable materials (for example, hydrogen, ammonia, urea, and methane) and chemical products, and valuable materials can be efficiently and inexpensively produced from the wastewater of the plant 10‴.

Reference Signs List

[0045]

1, 1′, 1″, 1‴ Hydrogen and ammonia production system
10, 10‴ Plant
11 Combustion chamber (combustion furnace)
12 Ammonia supply device
13 Dust collecting device
14 Wet-type treatment device
15 Stack
16 Boiler
18 Carbon dioxide separation device
19 Exhaust gas treatment device
20, 20′, 20″, 20‴ Valuable material generation facility
21 First ammonia recovery device
22 Second ammonia recovery device
23 First pH adjuster supply device
24 Second pH adjuster supply device
25 Flocculant supply device
26 Flocculation treatment tank
27 Ion removal device
28 Water electrolysis device
31 First circulation path (circulation path)
32 Second circulation path
33 Urea production device
34 Methanation device
40 General wastewater treatment device
41 Ammonia utilization equipment
42 Hydrogen utilization equipment
43 Urea utilization equipment
44 Methane gas utilization equipment
50 Pure water production device
51 Additive supply device

52 Steam drum
53 Heat recovery device
54 Steam turbine
55 Generator
56 Condenser
57 Deaerator
60 First flow path
61 Second flow path
62 Control valve
63 Control device
64 Ammonia concentration meter
65 Flow meter
66 Ammonia concentration meter
67 Flow meter
F1 Wastewater from exhaust gas treatment
F2 Steam
F3 Boiler blowdown water
F4 First concentrated ammonia solution
F5 Wastewater
F6 Wastewater from flocculation
F7 Component of scale
F8 Second concentrated ammonia solution
F9 Wastewater
F10 Concentrated ionic solution
F11 Permeated water
F12 Hydrogen
F13 Carbon dioxide
F14 Urea
F15 Methane
F16 Plant wastewater
P1 First position
P2 Second position
P3 Third position
P4 Fourth position
P5 Fifth position