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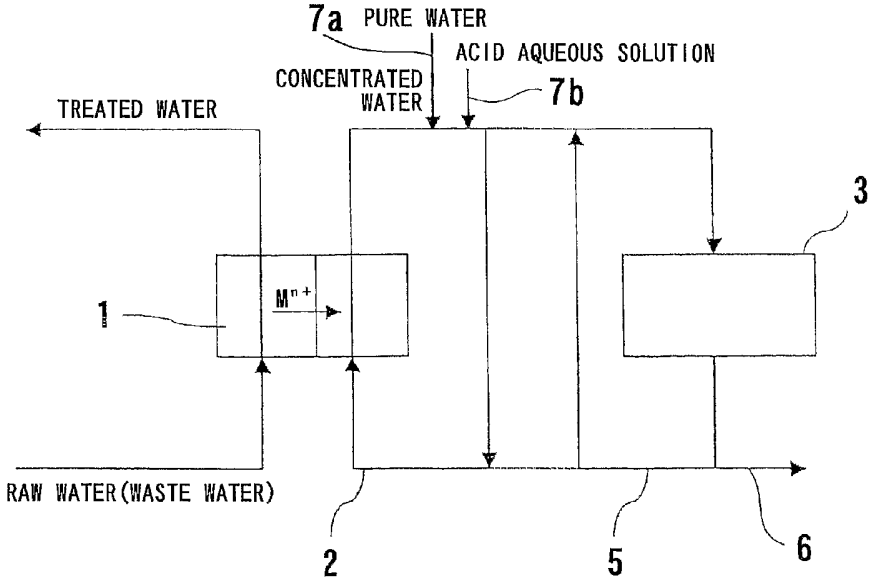
(54) Title: APPARATUS AND METHOD FOR TREATING WASTE WATER



(57) Abstract: An apparatus for continuously removing metal ions from waste water to recover solid metal includes a metal ion separation and concentration unit (1) operable to separate the metal ions and the coexistent cations from waste water to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations, a concentration system (2) operable to supply the concentrated water to the unit (1) to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations, a recovery system (4) having an electrolytic deposition unit (3) operable to selectively recover the metal ions from the concentrated water having the further increased concentrations, and a metal ion reducing system (5) operable to produce concentrated water having a lowered concentration of the metal ions.

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DESCRIPTION

APPARATUS AND METHOD FOR TREATING WASTE WATER

Technical Field

The present invention relates to an apparatus and method for continuously removing metal ions from various kinds of waste water to recover solid metal.

Background Art

Various kinds of waste water, such as those produced in plating processes, semiconductor device fabrication processes, printed circuit board fabrication processes, or mines, contain valuable noble metal ions in relatively small quantities and heavy metal which is the subject of restrictions on its release to the surroundings in view of the environmental issue. Further, as a continuous fabrication process has been employed, there is a tendency that waste water is continuously produced.

In treatment of such waste water containing the noble metal and the heavy metal, it has been required to sufficiently recover the noble metal contained in the waste water, remove the heavy metal to such a degree that treated waste water becomes harmless enough to be released to the surroundings, and recover the removed heavy metal as needed. Additionally, it has been required to continuously treat such waste water.

In fabrication processes of semiconductor devices such as semiconductor integrated circuits, there has been an increasing demand for finer interconnects. However, the tendency toward the finer interconnects entails a signal delay problem due to interconnect resistance. Thus, in order to solve this problem, instead of aluminum or tungsten, copper has recently been used to form interconnects.

Specifically, as semiconductor chips such as central processing units (CPU) or dynamic random access memories (DRAM) have become more highly integrated, interconnect material used in the semiconductor chips has changed from aluminum into copper which has a lower electrical resistance than aluminum. Particularly, there is a tendency to use copper in forming interconnects having a minimum width of 0.13 μm or smaller.

Generally, it is difficult to etch a copper layer to form patterns of interconnects. Therefore, a semiconductor substrate is plated with copper by damascene process so that a copper layer is formed on the semiconductor substrate, and then chemical mechanical

polishing (CMP) or electrochemical polishing (ECP) is applied to polish a surface of the copper layer to thereby form interconnects on the semiconductor substrate.

FIGS. 12A through 12E show an example of a process of forming copper interconnects on a semiconductor substrate. As shown in FIG. 12A, a conductive layer 202 is formed on a semiconductor substrate 201 on which semiconductor devices have been formed, and an insulating film 203 of SiO_2 is deposited on the conductive layer 202. Contact holes 204 and interconnect grooves 205 are formed on the surface of the insulating film 203 by lithography etching technique or other method. Then, as shown in FIG. 12B, a barrier layer 206 is formed on the insulating film 203. The barrier layer 206 is made of metal such as Ta, TaN, TiN, WN, SiTiN, CoWP, CoWB, or metallic compound thereof. In a case of using electroplating to form a copper layer, as shown in FIG. 12C, a copper seed layer 207, which serves as a feeding layer in electroplating, is further formed on the barrier layer 206 by sputtering or the like. In a case of using electroless plating to form a copper layer, instead of the copper seed layer, a catalyst layer 207 is formed on the barrier layer 206 by pretreatment process.

Subsequently, as shown in FIG. 12D, electroplating or electroless plating is applied onto the surface of the copper seed layer or catalyst layer 207 to fill the contact holes 204 and the interconnect grooves 205 with copper and to deposit a copper layer 208 on the insulating film 203. Thereafter, the copper layer 208 on the insulating film 203 is removed by chemical mechanical polishing (CMP) or electrochemical polishing (ECP) so that the surface of the copper layer 208 in the contact holes 204 and the interconnect grooves 205 is substantially flush with the surface of the insulating film 203. In this manner, as shown in FIG. 12E, interconnects comprising the copper seed layer or catalyst layer 207, and the copper layer 208 are formed on the surface of the insulating film 203.

A large amount of waste water containing copper ions is continuously produced in the copper plating process, e.g., the electroplating process or the electroless plating process, in a semiconductor device fabrication process, and in a chemical mechanical polishing (CMP) process and an electrochemical polishing (ECP) process for microchips having integrated circuits.

With respect to an allowable limit of copper ions contained in waste water, a maximum concentration of copper ions is restricted to not more than 3.0 mg/l in Japan. In the United States, a concentration of copper ions is more strictly regulated than in

Japan. For example, a maximum concentration of copper ions is restricted to not more than 2.7 mg/l, an average concentration of copper ions per day is restricted to not more than 1.0 mg/l, and an average concentration of copper ions per year is restricted to not more than 0.4 mg/l. Therefore, there has been strongly required to provide technology capable of efficiently and continuously removing copper from waste water.

In a general type of semiconductor device fabrication plant, a CMP apparatus produces waste water having a maximum copper concentration of about 100 mg/l at a maximum flow rate of about 0.5 m^3/h. A single copper plating apparatus produces waste water having a maximum copper concentration of about 200 mg/l at a maximum flow rate of about 0.2 m^3/h. In average fabrication plants for semiconductor devices having copper interconnects, there may be provided about ten CMP apparatuses and about five copper plating apparatuses per a plant. In such a plant, the total flow rate of waste water containing copper becomes as high as about 220 m^3/day at the maximum, and the total amount of copper contained in the waste water becomes as much as about 22 kg-Cu/day at the maximum. Thus, there has been strongly required to efficiently and continuously recover copper from the waste water to reuse it in view of resource saving as well as environmental protection.

In conventional industries including a semiconductor device fabrication industry, waste water has been treated mainly by an integrated waste water treatment facility in which waste water is collected from various processes in a plant and is collectively treated. However, in a semiconductor device fabrication industry in which fabrication processes have been rapidly improved, there is a need to treat waste water discharged from respective processes on the spots, i.e., at locations where water has been used. The reason is as follows. Production systems have changed from conventional mass production into diversified few quantity production. Types of products are changed so frequently that variation of properties of waste water becomes wide. The conventional waste water treatment facility cannot sufficiently cope with the variation of properties of waste water. Additionally, a system in which waste water produced in respective processes is respectively treated can facilitate recovery and reuse of metal as compared to the conventional integrated waste water treatment facility.

The waste water treatment facility is also required to continuously treat waste water which is continuously produced in the plants. If the waste water treatment facility is required to intermittently operate for the reasons of operation management and

maintenance, a spare apparatus or a buffer tank for storing the waste water should be provided in the waste water treatment facility, resulting in large size and high cost.

Waste water containing metal ions is treated typically by the following three methods: (1) a precipitation method in which chemicals are added to waste water so as to form insoluble hydroxide or sulfide, (2) an ion exchange method in which metal ions are absorbed by an ion exchange resin, and (3) an electrolytic deposition method in which metal is deposited on a surface of a cathode due to electrochemical reaction.

In a case where a metal ion concentration is relatively high, the electrolytic deposition method is often used because metal can be recovered. In a case where a metal ion concentration is low, the ion exchange resin method or the precipitation method is often used. This is because, if waste water having a low metal ion concentration of less than 200 mg/l is to be directly treated by the electrolytic deposition method, an operating voltage of an electrolytic deposition cell is required to increase and current efficiency decreases.

Generally, a copper concentration of waste water produced in a CMP process or a copper plating process is as low as 200 mg/l or less. Therefore, the electrolytic deposition method has not been used for recovering copper from waste water. In the ion exchange resin method, copper is absorbed by the ion exchange resin and recovered as copper ion. In the coagulative precipitation method, copper is deposited and recovered in the form of hydroxide or oxide. Accordingly, in both methods, additional treatments are required to reuse the recovered copper.

The precipitation method can continuously treat waste water, but is problematic in that a large amount of chemicals is used and a secondary treatment is required to treat metal-containing sludge which is by-product. Particularly, when treating copper-containing waste water, copper hydroxide is deposited in large quantities. This sludge has a high water content, i.e., a small copper content per unit volume, and it is therefore difficult to reuse such sludge, i.e., copper hydroxide. Further, copper hydroxide, i.e., metal hydroxide, should be stored in such a manner that copper is not dissolved again and does not pollute the environment.

The ion exchange resin method can sufficiently absorb and remove metal ions, but is problematic in that a large amount of acid is required to regenerate the ion exchange resin which was saturated due to absorption and a secondary treatment is required to treat metal-containing concentrated waste water. Particularly, when treating

CMP process waste water containing a large amount of coexistent cations such as ammonium ions and potassium ions in addition to copper ions, a large amount of ion exchange resin is required and a large amount of regeneration waste water is produced. Further, this method cannot continuously treat waste water because of regenerating operation, and is therefore problematic in treating waste water which is continuously produced.

The electrolytic deposition method is a method of recovering metal by depositing metal ions dissolved in waste water onto a cathode. This method is easy to operate at a low cost, and has been used as a copper recovery method in technical scale for more than 100 years. However, this method has the following problems in treating semiconductor fabrication waste water, such as CMP waste water or rinsing water used in a plating apparatus, which has a low concentration and exhibits unstable properties.

The first problem is that, in order to carry out the electrolytic deposition in an industrial manner, metal should be stably (and preferably continuously) extracted from the electrolytic cell. If metal ions in waste water are copper ions, copper can be easily deposited by electrolysis in the form of powders or fine particles. Therefore, copper powders can be extracted from the electrolytic cell. However, in order to stably extract the copper powders, the deposition state of the copper powders should be kept constant, and scraping the copper powders off the cathode and extracting the copper powders from a cathode chamber should be carried out stably and continuously.

The second problem is that, in order to apply the electrolytic deposition to the waste water treatment, a concentration of metal ions contained in treated water, which is to be discharged through an outlet of the electrolytic cell, is required to stably decrease to a desired permissible concentration. If the concentration of metal ions contained in the treated water at the outlet of the electrolytic cell cannot stably decrease to the permissible concentration, the treated water should be returned to an inlet of the waste water treatment apparatus so that the concentration of the metal ions decreases to the permissible concentration. As a result, processes become complicated, the facility becomes large, and a treatment cost becomes high. Instead of returning the treated water to the inlet of the waste water treatment apparatus, an additional process such as an ion exchange resin process may be provided. However, in this case, the number of components of the facility increases, thus causing the facility to become large.

The third problem is the need to cope with cations coexisting with metal ions in

waste water. For example, CMP waste water may contain, in addition to copper ions, a large amount of cations such as ammonium ions and potassium ions which are not deposited by electrolysis. Further, rinsing water for use in plating may contain organic cations, serving as an additive for improving plating performance, which are not deposited by electrolysis.

These coexistent cations are dialyzed together with copper ions in a metal ion separation and concentration apparatus to move into concentrated water. However, unlike metal ions such as copper ions, the coexistent cations are not deposited by an electrolytic deposition apparatus, and are thus not removed from the waste water. Consequently, the concentration of the coexistent cations gradually increases in the concentrated water. When the concentration of the coexistent cations exceeds a permissible solubility, deposits are produced. Therefore, the concentration of the coexistent cations is required not to exceed a certain value.

The fourth problem is that, even if the concentrated water containing the coexistent cations is periodically discharged so that the concentration of the coexistent cations does not exceed a certain value, it is required to continuously treat the waste water which is continuously produced.

Disclosure of Invention

The present invention has been made in view of the above drawbacks. It is, therefore, an object of the present invention to provide a waste water treatment apparatus and a waste water treatment method which can continuously remove metal ions from various kinds of waste water even in a case where concentrated water containing coexistent cations is required to be periodically discharged.

For the purpose of solving the above drawbacks, the inventors of the present invention have developed from an extensive study an apparatus and method of recovering metal ions from waste water by utilizing a combination of an electrodialysis operation and an electrolytic deposition operation. Specifically, the inventors have developed an apparatus and method which can continuously treat waste water having metal ions and coexistent cations and can recover metal and treated water having a lowered concentration of the metal ions by the combination of a concentration system or concentration process for concentrating the metal ions and the coexistent cations, a recovery system or recovery process for recovering the metal ions, and a discharge

passage or discharge process for discharging concentrated water after recovering the metal ions.

In order to achieve the above objects, according to an aspect of the present invention, there is provided a waste water treatment apparatus for treating waste water having at least metal ions and coexistent cations to produce treated water having a lowered concentration of the metal ions and to recover the metal ions as metal. The apparatus comprises a metal ion separation and concentration unit operable to separate the metal ions and the coexistent cations from waste water by electrodialysis operation to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations, a concentration system operable to circulate and supply the concentrated water to the metal ion separation and concentration unit to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations, a recovery system having an electrolytic deposition unit operable to receive the concentrated water having the further increased concentrations of the metal ions and the coexistent cations and to selectively recover the metal ions, the recovery system being operable to circulate and supply the concentrated water having a lowered concentration of the metal ions to the metal ion separation and concentration unit, and a metal ion reducing system operable to circulate and supply the concentrated water having the increased concentration of the coexistent cations to the electrolytic deposition unit to produce concentrated water having a lowered concentration of the metal ions.

In a preferred aspect of the present invention, the waste water treatment apparatus further comprises a discharge passage through which the concentrated water having the lowered concentration of the metal ions produced by the metal ion reducing system is discharged out of the metal ion reducing system.

In a preferred aspect of the present invention, the concentration system, the recovery system, or the metal ion reducing system comprises supply passages for introducing pure water and an acid aqueous solution into the system.

In a preferred aspect of the present invention, the electrolytic deposition unit comprises a rotating electrolytic cell having an anode and a rotatable cathode. The anode is disposed outside the cathode. The rotating electrolytic cell is operable to deposit the metal on a surface of the cathode while rotating the cathode.

In a preferred aspect of the present invention, the waste water treatment

apparatus according to claim 4, wherein the electrolytic deposition unit further comprises a scraper disposed in contact with or adjacent to the rotatable cathode so that the scraper scrapes off the metal deposited on the surface of the cathode.

In a preferred aspect of the present invention, the metal removed from the surface of the cathode by the scraper is delivered to a filter together with the concentrated water and captured by the filter.

In a preferred aspect of the present invention, the concentration system and the metal ion reducing system can operate simultaneously.

In a preferred aspect of the present invention, the concentrated water having the lowered concentration of the metal ions is discharged through the discharge passage while the recovery system is operating.

In a preferred aspect of the present invention, the waste water containing the metal ions is produced in a semiconductor fabrication apparatus or pretreated after being produced in a semiconductor fabrication apparatus.

In a preferred aspect of the present invention, the metal ions contained in the waste water are copper ions produced in a semiconductor fabrication apparatus for forming copper interconnects.

According to another aspect of the present invention, there is provided a waste water treatment method for treating waste water having at least metal ions and coexistent cations to produce treated water having a lowered concentration of the metal ions and to recover the metal ions as metal. The method comprises a metal ion separation and concentration process for separating the metal ions and the coexistent cations from waste water by electrodialysis operation in a metal ion separation and concentration unit to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations, a concentration process for circulating and supplying the concentrated water to the metal ion separation and concentration unit to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations, a recovery process in which an electrolytic deposition unit receives the concentrated water having the further increased concentrations of the metal ions and the coexistent cations to selectively recover the metal ions, and the concentrated water having a lowered concentration of the metal ions is circulated and supplied to the metal ion separation and concentration unit, and a metal ion reducing process for circulating

and supplying the concentrated water having the increased concentration of the coexistent cations to the electrolytic deposition unit to produce concentrated water having a lowered concentration of the metal ions.

In a preferred aspect of the present invention, the waste water treatment method further comprises a discharge process in which the concentrated water having the lowered concentration the metal ions produced by the metal ion reducing process is discharged out of a system in which the waste water treatment method is carried out.

In a preferred aspect of the present invention, the waste water treatment method further comprises a replenishment process for replenishing the system with pure water and an acid aqueous solution after the discharge process.

In a preferred aspect of the present invention, the electrolytic deposition unit comprises a rotating electrolytic cell having an anode and a rotatable cathode. The anode is disposed outside the cathode. The rotating electrolytic cell is operable to deposit the metal on a surface of the cathode while rotating the cathode.

In a preferred aspect of the present invention, the metal deposited on the surface of the cathode is scraped off by a scraper disposed in contact with or adjacent to the rotatable cathode.

In a preferred aspect of the present invention, the metal removed from the surface of the cathode by the scraper is delivered to a filter together with the concentrated water and captured by the filter.

In a preferred aspect of the present invention, the concentration process and the metal ion reducing process can be performed simultaneously.

In a preferred aspect of the present invention, the discharge process is performed during the recovery process to discharge the concentrated water having the lowered concentration of the metal ions.

In a preferred aspect of the present invention, the waste water containing the metal ions is produced in a semiconductor fabrication apparatus or pretreated after being produced in a semiconductor fabrication apparatus.

In a preferred aspect of the present invention, the metal ions contained in the waste water are copper ions produced in a semiconductor fabrication apparatus for forming copper interconnects.

According to the present invention, the concentration of the coexistent cations in the waste water can be kept below a predetermined value. Even if the concentrated

water containing the coexistent cations is periodically discharged, the waste water, which is continuously produced, can be continuously treated.

Further, according to the present invention, only a single rotating electrolytic cell is required to continuously introduce the waste water having the coexistent cations and a lowered concentration of the metal ions into the metal ion separation and concentration unit, and to discharge the coexistent cations and recover the metal.

Brief Description of Drawings

FIGS. 1A and 1B are schematic views showing a basic concept of a waste water treatment apparatus according to an embodiment of the present invention;

FIG. 2 is a treatment flow view showing the waste water treatment apparatus which can perform continuous operation according to the basic concept of the embodiment shown in FIGS. 1A and 1B;

FIG. 3 is a treatment flow view showing the waste water treatment apparatus which can perform continuous operation according to the basic concept of the embodiment shown in FIGS. 1A and 1B;

FIG. 4 is a treatment flow view showing the waste water treatment apparatus which can perform continuous operation according to the basic concept of the embodiment shown in FIGS. 1A and 1B;

FIG. 5 is a treatment flow view showing the waste water treatment apparatus which can perform continuous operation according to the basic concept of the embodiment shown in FIGS. 1A and 1B;

FIG. 6 is a view showing changes in metal ion concentration and coexistent cation concentration based on the treatment flow views shown in FIGS. 2 through 5;

FIG. 7 is a schematic view showing an electrolytic deposition unit according to an embodiment of the present invention;

FIG. 8 is a schematic view showing an example in which raw water is introduced in a tangential direction of a cylindrical electrolytic cell so that the raw water revolves;

FIG. 9 is a schematic view showing an electrolytic deposition unit according to another embodiment of the present invention;

FIG. 10 is a schematic view showing an electrolytic deposition unit according to still another embodiment of the present invention;

FIG. 11 is a schematic view showing an electrolytic deposition unit according to still another embodiment of the present invention; and

FIGS. 12A through 12E show an example of a process of forming interconnects on a semiconductor substrate.

Best Mode for Carrying Out the Invention

A basic concept and embodiments of the present invention will be described below with reference to the drawings. In the drawings, like or corresponding parts are denoted by the same reference numerals.

FIGS. 1A and 1B are schematic views showing a basic concept of a waste water treatment apparatus according to an embodiment of the present invention. As shown in FIGS. 1A and 1B, the waste water treatment apparatus comprises a metal ion separation and concentration unit (an electrodialyser) 1, a concentration system 2 (see FIG. 1A), a recovery system 4 (see FIG. 1B), and a metal ion reducing system 5 (see FIG. 1A). The metal ion separation and concentration unit 1 serves to separate metal ions and coexistent cations from waste water by an electrodialysis operation to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations. The concentration system 2 serves to circulate and supply the concentrated water to the metal ion separation and concentration unit 1 to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations. The recovery system 4 has an electrolytic deposition unit 3 for receiving the highly concentrated water, having the further increased concentrations of the metal ions and the coexistent cations, to selectively recover the metal ions, and circulates and supplies the concentrated water having a lowered concentration of the metal ions to the metal ion separation and concentration unit 1. The metal ion reducing system 5 serves to circulate and supply the concentrated water having the increased concentration of the coexistent cations to the electrolytic deposition unit 3 so as to produce concentrated water having a lowered concentration of the metal ions. In this specification, the concentrated water means water which has been treated by the metal ion separation and concentration unit 1.

As shown in FIG. 1A, the waste water treatment apparatus further comprises a discharge passage 6 through which the concentrated water, having the lowered concentration of the metal ions, produced by the metal ion reducing system 5 is

discharged out of the system. As shown in FIGS. 1A and 1B, the concentration system 2, the recovery system 4, or the metal ion reducing system 5 of the waste water treatment apparatus comprises a supply passage 7a which can introduce pure water into the system, and a supply passage 7b which can introduce an acid aqueous solution into the system.

FIGS. 2 through 5 are treatment flow views showing the structure of the waste water treatment apparatus which can perform continuous operation according to the basic concept of the present invention shown in FIGS. 1A and 1B. FIG. 6 is a view showing changes in the metal ion concentration and the coexistent cation concentration based on the treatment flow views shown in FIGS. 2 through 5. The waste water treatment apparatus according to embodiments shown in FIGS. 2 through 5 comprises the metal ion separation and concentration unit 1, the concentration system 2, the electrolytic deposition unit 3, the recovery system 4, the metal ion reducing system 5, two tanks T1 and T2, two pumps P1 and P2, the discharge passage 6, and the supply passages 7a and 7b.

FIG. 2 shows the treatment flow illustrating a concentration process and a metal ion reducing process. The concentration process selectively separates the metal ions and the coexistent cations from the raw water (waste water) by the electrodialysis operation to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations. The metal ion reducing process lowers the concentration of the metal ions in the concentrated water in order to allow the concentrated water remaining in the waste water treatment apparatus to be released to the exterior.

In the concentration process, the concentrated water circulates through the concentration system 2 extending through the metal ion separation and concentration unit 1 and the first tank T1. In the metal ion reducing process, the concentrated water having the increased concentration of the coexistent cations circulates through the metal ion reducing system 5 extending through the electrolytic deposition unit 3 and the second tank T2.

In order to efficiently deposit metal on a cathode by the electrolytic deposition operation, the concentration of the metal ions in the concentrated water is preferably not less than 100 mg/l, more preferably not less than 200 mg/l because a high current efficiency can be achieved. Further, in order to maintain a state of the deposited metal

constant (for example, a powdered state), it is preferable that the concentration of the metal ions in the concentrated water is kept substantially constant. Furthermore, in order not to produce metal hydroxide and metal oxide in the concentrated water, the pH of the concentrated water is required to be on the acid side, preferably in the range of 1 to 4. Sulfuric acid, which does not cause harmful electrode reaction, is preferably used as an acid to be added to the concentrated water.

In the electrodialysis operation, ions migrate from the raw water side to the concentrated water side through the ion exchange membrane, so that the treated water having ion concentration lowered to 1 mg/l or less and the concentrated water having increased ion concentration are produced. In this operation, if the concentration of the concentrated water increases to 1000 mg/l or more, the ions may migrate in reverse from the concentrated water to the raw water due to concentration diffusion, resulting in an increased concentration of the metal ions in the treated water. Such reverse migration is not preferable.

Accordingly, when treating raw water (waste water) by the electrodialysis operation so as to produce treated water having lowered concentration of the metal ions and to produce concentrated water having the concentrated metal ions, and when using the electrolytic deposition operation so as to recover the powdery metals from the concentrated water, it is preferable to add pure water and sulfuric acid to the concentrated water so that the pH of the concentrated water is in the range of 1 to 4. Further, the concentration of the metal ions in the concentrated water is preferably in the range of 100 to 1000 mg/l, more preferably in the range of 200 to 500 mg/l. By appropriately adjusting the pH and the concentration of the metal ions as described above, the current efficiency of the electrolytic deposition unit can be kept at not less than 80 % while the concentration of the metal ions in the treated water is kept at not more than 0.5 mg/l.

Before discharging the concentrated water remaining in the waste water treatment apparatus to the exterior thereof through the discharge passage 6, the concentration of the metal ions is required to be lowered to the permissible limit or less. As the concentrated water is circulated and supplied to the electrolytic deposition unit, the concentration of the metal ions is gradually lowered to such a level that the concentrated water can be released to the exterior of the treatment apparatus. When the concentration of the metal ions in the concentrated water is lowered to 100 mg/l or less, the current efficiency is gradually lowered. However, this is a temporary operation for

the purpose of discharging the concentrated water remaining in the apparatus, and therefore does not cause any problem.

It is needless to say that the metal ion reducing process is not required to be carried out when the treatment apparatus does not retain the concentrated water to be discharged, e.g., when the treatment apparatus starts operation.

FIG. 3 shows the treatment flow illustrating a recovery process, a discharge process, and a replenishment process. The recovery process serves to selectively separate metal ions and coexistent cations from raw water (waste water) by the electrodialysis operation to produce treated water having lowered concentrations of the metal ions and the coexistent cations. The recovery process also serves to recover metal using the electrolytic deposition unit 3. Specifically, the electrolytic deposition unit 3 deposits the metal by an amount corresponding to the metal ions separated by the metal ion separation and concentration unit 1 from the concentrated water having the increased concentrations of the metal ions and the coexistent cations. The discharge process serves to discharge the concentrated water, whose metal ion concentration has been lowered by the metal ion reducing process, to the exterior of the system through the discharge passage 6. The replenishment process serves to replenish the system with pure water and a sulfuric acid aqueous solution.

In the recovery process, the concentrated water circulates through the recovery system 4 extending through the metal ion separation and concentration unit 1, the electrolytic deposition unit 3, and the first tank T1. In the discharge process, the concentrated water having the lowered concentration of the metal ions is discharged from the second tank T2 to the exterior of the system through the discharge passage 6. In the replenishment process, the second tank T2 is replenished with predetermined amounts of the pure water and the sulfuric acid aqueous solution.

The concentration of the metal ions in the concentrated water increases in the concentration process to such a degree that the metal can be efficiently deposited by the electrolytic deposition unit, and is enriched by the metal ion separation and concentration unit. Therefore, by appropriately controlling current value of the electrolytic deposition unit, the metal ions can be easily recovered by the electrolytic deposition unit while the concentration of the metal ions in the concentrated water is kept substantially constant. It is also possible to operate the electrolytic deposition unit in such a manner as to increase or decrease the concentration of the metal ions in the concentrated water by

controlling the current value of the electrolytic deposition unit within the range where the electrolytic deposition unit can efficiently operate.

It is preferable that the electrolytic deposition unit comprises a rotating electrolytic cell having a scraper therein because the rotating electrolytic cell is suitable for continuous operation. With this structure, the metal is deposited on a surface of a rotating cathode, and is scraped off the cathode by the scraper. Metal powders, which were removed from the surface of the cathode, are captured by a bag filter (BF). A plurality of bag filters may be disposed in parallel. A bypass line may be provided beside the bag filter, so that a bypass operation can be performed so as to facilitate the replacement of the bag filter.

The coexistent cations in the concentrated water are not deposited in the electrolytic deposition unit. Therefore, the concentration of the coexistent cations in the concentrated water gradually increases. If the concentration of the coexistent cations exceeds the solubility, the coexistent cations are deposited in the solution. Such deposited coexistent cations are undesirable because they may be mixed into the metal to be recovered and may cause clogging of pipes.

Therefore, the operation of the recovery process is preferably performed within the range where the concentration of the coexistent cations does not exceed the solubility. In this case, when the concentration of the coexistent cations approaches the solubility, the recovery operation is stopped.

The concentrated water having the lowered concentration of the metal ions may be discharged from the system all at once, or may be discharged while being gradually mixed with the treated water. If the concentration of the metal ions is not lowered sufficiently, the concentrated water is discharged while being gradually mixed with the treated water, so that the concentration of the metal ions can be lowered below the permissible value.

After the concentrated water is discharged, the system is replenished with the pure water and the sulfuric acid aqueous solution, so that the system is on standby in preparation for the next concentration process.

FIG. 4 shows the treatment flow using another system in the apparatus to perform the same operation as the treatment flow shown in FIG. 2.

In the concentration process shown in this flow, the concentrated water circulates through the concentration system 2 extending through the metal ion separation

and concentration unit 1 and the second tank T2. In the metal ion reducing process, the concentrated water having the increased concentration of the coexistent cations circulates through the metal ion reducing system 5 extending through the electrolytic deposition unit 3 and the first tank T1.

FIG. 5 shows the treatment flow using another system in the apparatus to perform the same operation as the treatment flow shown in FIG. 3. In the concentration process shown in this flow, the concentrated water circulates through the recovery system 4 extending through the metal ion separation and concentration unit 1, the electrolytic deposition unit 3, and the second tank T2. In the discharge process, the concentrated water having the lowered concentration of the metal ions is discharged from the first tank T1 to the exterior of the system through the discharge passage 6. In the replenishment process, the second tank T1 is replenished with predetermined amounts of the pure water and the sulfuric acid aqueous solution.

FIGS. 2 through 5 show examples illustrating the pipe systems according to the basic concept shown in FIGS. 1A and 1B, and do not limit the present invention. In these drawings, measuring instruments and valves are not illustrated.

FIG. 6 schematically shows the changes in the concentrations of the metal ions and the coexistent cations inside the tank T1 and the tank T2 of the concentration process, the recovery process, the metal ion reducing process, the discharge process, and the replenishment process shown in FIGS. 2 through 5.

In the concentration process, the concentrations of the metal ions and the coexistent cations inside the tank gradually increase until the concentration of the metal ions reaches a value suitable for the electrolytic deposition. The concentration of the coexistent cations also increases. Some kinds of waste water, such as Cu-CMP waste water, contain potassium ions and ammonium ions as the coexistent cations. The potassium ions and the ammonium ions are not deposited by the electrodialysis operation, and the concentrations of these ions in the treated water are not required to be lowered to 1 mg/l or less. Therefore, it is not necessary to take influence of the concentration of the coexistent cations into consideration in the concentration process.

In the recovery process, the electrolytic deposition unit 3 lowers the concentration of the metal ions in the tank by an amount that has been enriched by the metal ion separation and concentration unit 1. Therefore, the concentration is kept substantially constant.

The concentration of the coexistent cations in the tank cannot be lowered by the electrolytic deposition unit 3. Accordingly, the concentration gradually increases until it reaches an upper limit concentration which is set depending on types of coexistent cations.

In the metal ion reducing process, the concentration of the metal ions in the tank is gradually lowered to such a level that the metal ions can be released to the exterior of the treatment apparatus. The concentration of the coexistent cations does not change.

In the discharge process, the concentrated water is simply discharged from the tank. Therefore, the concentrations of the metal ions and the coexistent cations in the tank do not change.

In the replenishment process, since the tank is replenished with the pure water and the sulfuric acid aqueous solution, the metal ion concentration and the coexistent cation concentration in the tank are diluted and thus lowered.

Next, the electrolytic deposition unit 3 according to embodiments of the present invention will be described with reference to FIGS. 7 through 11. In the drawings, like or corresponding parts are denoted by the same reference numerals.

FIG. 7 is a schematic view showing the electrolytic deposition unit according to an embodiment of the present invention.

As shown in FIG. 7, the electrolytic deposition unit 3 comprises an electrolytic cell 12, a substantially cylindrical cathode 13 disposed in the electrolytic cell 12, a cation exchange membrane 14 disposed in the electrolytic cell 12 and located outside the cathode 13, and an anode 16 surrounding an outer circumferential surface of the cation exchange membrane 14. A cation exchanger 15 is disposed between the cation exchange membrane 14 and the anode 16.

A rotational shaft 17 is provided on the cathode 13 so that the cathode 13 is rotated by a motor (not shown) coupled to the rotational shaft 17. The anode 16 is made of gas-permeable material. A direct-current power source (not shown) allows direct current to flow between the cathode 13 and the anode 16. A scraper 18 is disposed adjacent to the cathode 13 for scraping off a part of metal deposited on the surface of the cathode 13. The scraper 18 may be disposed in contact with the cathode 13. The inside of the electrolytic cell 12 is divided by the cation exchange membrane 14 into an anode chamber 19 and a cathode chamber 20. A circulation line 21 extends from the bottom of the electrolytic cell 12. A circulation pump 22 and a bag filter 23 are

provided on the circulation line 21.

In the electrolytic deposition unit 3 shown in FIG. 7, raw water (waste water to be treated) is firstly introduced into the cathode chamber 20 formed between the rotating cathode 13 and the cation exchange membrane 14. The direct current is applied between the cathode 13 and the anode 16, so that metal ions in the waste water are deposited on the surface of the cathode 13 in the form of powder metal or acicula metal. A part of the deposited metal is removed from the surface of the cathode 13 by the scraper 18 disposed adjacent to the surface of the cathode 13. The metal removed from the cathode 13 is led into the circulation line 21 provided on the bottom of the electrolytic cell 12, and is then recovered by the bag filter 23. Since the surface of the cathode 13 is scraped by the scraper 18 at all times, the condition of the surface of the cathode 13 is kept constant. Accordingly, a state of the metal deposited on the cathode 13 can be easily controlled by adjusting an electrolyte solution, a current density, a rotational speed of the cathode 13, and the like.

The cation exchanger 15 is disposed between the gas-permeable anode 16 and the cation exchange membrane 14, and pure water is supplied to the anode chamber 19 in which the anode 16 is disposed. With this structure, although an oxygen gas is produced due to pure water electrolysis occurring on the surface of the anode 16 which is in contact with the cation exchanger 15, the oxygen gas does not enter the cathode chamber 20 because the oxygen gas is intercepted by the cation exchange membrane 14. Accordingly, the metal removed from the cathode 13 is not dissolved again and is not formed into the metal ions. Additionally, since the waste water does not come into direct contact with the anode 16, even if the waste water is highly corrosive, the anode 16 does not deteriorate. After the metal ions are recovered as metal, the water is extracted from the cathode chamber 20 disposed between the cathode 13 and the cation exchange membrane 14.

Instead of providing the above-mentioned structure in which the anode chamber 19 and the cathode chamber 20 are isolated from each other as shown in FIG. 7, the anode chamber 19 and the cathode chamber 20 may communicate with each other as shown in FIG. 11. In this structure, a pressurized inert gas containing no oxygen is supplied to the cathode chamber 20 so as to form a gas flow running from the cathode chamber 20 to the anode chamber 19. Such a gas flow prevents oxygen, which is produced in the anode chamber 19, from entering the cathode chamber 20, and can

therefore prevent the removed metal from being dissolved again. Nitrogen gas or argon gas is suitably used as the inert gas to be supplied.

In the electrolytic deposition unit 3 shown in FIG. 7, the anode 16 and the cation exchanger 15 are in contact with each other in the anode chamber 19 in the presence of pure water. Therefore, under electric potential gradient, pure water electrolysis easily occurs on the anode surface which is in contact with the cation exchanger 15, thereby producing an oxygen gas and H^+ ions. The oxygen gas passes through the anode 16, which is a gas-permeable electrode, to enter the anode chamber 19 behind the anode 16, and is then discharged to the exterior of the unit. The H^+ ions migrate through the cation exchanger 15 and the cation exchange membrane 14 into the cathode chamber 20 due to electric potential gradient. Since the pure water is consumed in electrolysis, replenishment of pure water is required. Pure water can be supplied in various ways. For example, pure water may be supplied in such an amount that excessive pure water overflows from the anode chamber 19, or pure water may be circulated and supplied.

The metal is reduced to be deposited on the surface of the cathode 13. As the concentration of the metal ions becomes low, the H^+ ions are also reduced to a hydrogen gas. The hydrogen gas produced on the surface of the cathode 13 is discharged out of the system. The hydrogen gas may be discharged together with a diluent gas which is introduced to the system from outside, or may be introduced into the anode chamber 19 and then extracted from the anode chamber 19 together with the oxygen gas produced on the surface of the anode 16. The diluent gas is preferably such that oxygen is not dissolved in the cathode liquid. Nitrogen gas or inert argon gas is preferably used as the diluent gas. The cathode 13 may have a smooth surface for the purpose of improving the capability of removal of the deposited metal. Further, the cathode 13 may have a large surface area for the purpose of decreasing current density so that the metal can be deposited in the form of acicula or powder. For example, the surface of the cathode 13 may have concave portions and convex portions. In this manner, various types of surfaces can be applied.

In view of efficiency and uniformity of deposition of the metal on the surface of the cathode 13, it is preferable to sufficiently agitate the raw water in the electrolytic cell 12. The agitation of the waste water (raw water) can be made, for example, by increasing the rotational speed of the cathode 13 or by introducing the waste water in a tangential direction of the cathode 13 so that the waste water revolves.

FIG. 8 is a schematic view showing an example in which the raw water is introduced in the tangential direction of the cylindrical electrolytic cell 12 and the cylindrical cation exchange membrane 14 so that the raw water revolves.

A space between the cation exchange membrane 14 and the anode 16 is filled with the cation exchanger 15. As the ion exchanger, it is possible to use a known ion exchange resin or an ion exchange resin formed by a binder. It is also possible to use an ion exchange resin bonded to a porous base, e.g., sponge, or a textile base. However, as the ion exchanger, it is preferable to use a fibrous material comprising polymer fibrous substrates to which ion-exchange groups are introduced by graft polymerization. The substrates of polymer fibers to be grafted may either be single fibers of a polyolefin such as polyethylene or polypropylene, or composite fibers comprising a core portion and a sheath portion in which the core portion and the sheath portion are made of different polymers respectively. The ion exchanger, which is obtained by introducing ion-exchange groups into the composite fibers by a radiation-induced graft polymerization, is excellent in the ion-exchange capacity and can be produced with a uniform thickness, and is therefore desirable to be used. The ion-exchange fibrous material may be in the form of a woven fabric, nonwoven fabric, or the like.

The radiation-induced graft polymerization is a technique for introducing a monomer into polymer substrates by irradiating the polymer substrates with radiation rays so as to produce a radical which reacts with the monomer.

Radiation rays usable for the radiation-induced graft polymerization include α -rays, β -rays, γ -rays, electron beam, ultraviolet rays, and the like. Of these, γ -rays or electron beam may preferably be used in the present invention. As the radiation-induced graft polymerization, there are a pre-irradiation graft polymerization comprising previously irradiating graft substrates with radiation rays and then contacting the substrates with a grafting monomer, and a co-irradiation method in which irradiation of radiation rays is carried out in the co-presence of substrates and a grafting monomer. Both of these methods may be employed in the present invention. Further, depending upon the manner of contact between a monomer and substrates, there are polymerization methods such as a liquid-phase graft polymerization method in which polymerization is effected while substrates are immersed in a monomer solution, a gas-phase graft polymerization method in which polymerization is effected while substrates are in contact with vapor of monomer, and an immersion gas-phase graft polymerization

method in which substrates are firstly immersed in a monomer solution and then removed from the monomer solution and a polymerization is effected in a gas phase. Either method of polymerization may be employed in the present invention.

The ion-exchange groups to be introduced into fibrous substrates such as a nonwoven fabric are not particularly limited. Various kinds of cation-exchange groups can be used. For instance, usable cation-exchange groups include strongly acidic cation-exchange groups such as sulfo group, moderately acidic cation-exchange groups such as phosphoric group, and weakly acidic cation-exchange groups such as carboxy group.

These various ion-exchange groups can be introduced into fibrous substrates by subjecting a monomer having such an ion-exchange group to graft polymerization, preferably radiation-induced graft polymerization, or by subjecting a polymerizable monomer having a group that are changeable into an ion-exchange group, to graft polymerization, followed by conversion of that group into the ion-exchange group.

Monomers having an ion-exchange group usable for this purpose may include acrylic acid (AAc), methacrylic acid, sodium styrenesulfonate (SSS), sodium methallylsulfonate, sodium allylsulfonate, sodium vinylsulfonate, vinylbenzyl trimethylammonium chloride (VBTAC), diethylaminoethyl methacrylate, and dimethylaminopropylacrylamide. Sulfo group as a strongly acidic cation-exchange group, for example, may be introduced directly into substrates by carrying out radiation-induced graft polymerization in which sodium styrenesulfonate is used as a monomer. The monomer having groups that can be converted into ion-exchange groups may include acrylonitrile, acrolein, vinylpyridine, styrene, chloromethylstyrene, and glycidyl methacrylate (GMA). Sulfo group as a strongly acidic cation-exchange group, for example, may be introduced into substrates in such a manner that glycidyl methacrylate is introduced into the substrates by radiation-induced graft polymerization, and then react with a sulfonating agent such as sodium sulfite.

FIG. 9 is a schematic view showing an electrolytic deposition unit according to another embodiment of the present invention. In the embodiment shown in FIG. 7, the treated water is extracted from the cathode chamber 20. In this embodiment shown in FIG. 9, the treated water is extracted after passing through the bag filter 23. Other structures of this embodiment shown in FIG. 9 are the same as those of the embodiment shown in FIG. 7.

FIG. 10 is a schematic view showing an electrolytic deposition unit according to still another embodiment of the present invention. In the embodiment shown in FIG. 10, the treated water extracted from the cathode chamber 20 is stored in a storage vessel 24. The treated water stored in the storage vessel 24 can be returned by a pump 25 to the cathode chamber 20 disposed between the cathode 13 and the cation exchange membrane 14. Other structures of this embodiment are the same as those of the embodiment shown in FIG. 7.

Next, a specific example of the electrolytic deposition unit 3 shown in FIG. 7 will be described.

The anode 16 is formed from a plate-like lath metal which is made of Ti plated with Pt. The cathode 13 is made of SUS 304 and has a smooth surface. The rotational speed of the cathode 13 is in the range of 1 to 500 rpm (min^{-1}). Current density on the surface of the cathode 13 is in the range of 1 to 10 A/dm^2. The inner surface and a water-surface portion of the outer surface of the cathode 13 are coated with Teflon (registered trademark) resin so that the metal can be deposited only on a predetermined portion of the outer surface. Although the cathode liquid (raw water) containing metal ions can be supplied in a batch manner, it is preferable that the cathode liquid is continuously supplied to and extracted from the cathode chamber 20. This is because supplying the cathode liquid in this manner can suppress the fluctuation of the concentration of the metal ions in the cathode chamber 20, and is therefore preferable in view of electrolytic deposition conditions. FIG. 7 also shows one example of the manner of supplying the cathode liquid. Specifically, the cathode liquid (raw water) is supplied to the outer side of the rotating cathode 13 from above so that the cathode liquid overflows from a top portion of a weir provided inside the rotating cathode 13. Supplying the cathode liquid in this manner is preferable because the metal powders scraped off by the scraper 18 do not flow out of the cathode chamber 20. It is further preferable to supply the cathode liquid from the side surface of the cathode chamber 20 in the tangential direction of the cathode 13 so as to form a counterflow against the rotational direction of the rotating cathode 13 because a thickness of a diffusion layer on the surface of the cathode 13 can be reduced.

The metal powders 30, which were scraped off by the scraper 18, are delivered by a circulating pump flow through an outlet nozzle disposed on the bottom of the cathode chamber 20, and are captured by the bag filter 23. Hole diameter of the bag

filter 23 is in the range of 1 to 10 μm.

The anode 16 is preferably made of materials used for an insoluble electrode. For example, titanium plated with platinum is used to form the anode 16. The anode 16 preferably has a porous structure such as mesh or lath mesh (expanded metal). The cathode 13 is preferably made of stainless steel. The rotational speed of the cathode 13 is in the range of 1 to 500 rpm (min^{-1}), preferably in the range of 50 to 200 rpm (min^{-1}). A distance between the cathode 13 and the anode 16 can be selected within a range of 20 to 50 mm. Current density on the surface of the cathode 13 is preferably in the range of 2 to 3 A/dm^2. Hole diameter of the bag filter 23 is preferably in the range of 1 to 10 μm. An outlet port of the treated water may be provided on the cathode chamber 20 or the outlet of the bag filter 23. The scraper 18 is preferably made of resin or ceramic having an excellent chemical resistance. A distance between the scraper 18 and the cathode 13 is preferably in the range of 0.5 to 5 mm.

It is preferable that raw water (i.e., water to be treated) is pretreated before being supplied to the apparatus. Specifically, substances which have negative influence on electrolytic deposition are preferably removed or separated from the raw water, and the raw water is preferably concentrated in order to improve the efficiency of electrolytic deposition, as needed. For example, an activated carbon and an ion exchange resin may be used to pretreat the raw water. Specifically, the activated carbon is used to decompose an oxidizing agent, such as hydrogen peroxide, contained in the waste water, and then the ion exchange resin is used to absorb metal ions so as to remove them from the raw water. The ion exchange resin can be regenerated by acid. According to this pretreatment process, an acid solution of 0.5 to 5 g/L, which is suitable for electrolytic deposition, can be obtained. Additionally, as shown in an earlier Japanese patent application No. 2003-125889 filed by the applicants of the present invention, the raw water may be pretreated by a combination of a platinum-supported catalyst and electrodialysis. This pretreatment process is more preferable because an acid solution of about 0.5 to 1 g/L, which is suitable for electrolytic deposition, can be continuously obtained. Depending on the properties of the raw water, the pretreatment may not be required. In such a case, the waste water can be directly introduced into the electrolytic deposition process.

Industrial Applicability

The present invention is suitable for use in a waste water treatment apparatus and method for continuously removing metal ions from various kinds of waste water to recover solid metal.

CLAIMS

1. A waste water treatment apparatus for treating waste water having at least metal ions and coexistent cations to produce treated water having a lowered concentration of the metal ions and to recover the metal ions as metal, said apparatus comprising:

a metal ion separation and concentration unit operable to separate the metal ions and the coexistent cations from waste water by electrodialysis operation to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations;

a concentration system operable to circulate and supply the concentrated water to said metal ion separation and concentration unit to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations;

a recovery system having an electrolytic deposition unit operable to receive the concentrated water having the further increased concentrations of the metal ions and the coexistent cations and to selectively recover the metal ions, said recovery system being operable to circulate and supply the concentrated water having a lowered concentration of the metal ions to said metal ion separation and concentration unit; and

a metal ion reducing system operable to circulate and supply the concentrated water having the increased concentration of the coexistent cations to said electrolytic deposition unit to produce concentrated water having a lowered concentration of the metal ions.

2. The waste water treatment apparatus according to claim 1, further comprising a discharge passage through which the concentrated water having the lowered concentration of the metal ions produced by said metal ion reducing system is discharged out of said metal ion reducing system.

3. The waste water treatment apparatus according to claim 1 or 2, wherein said concentration system, said recovery system, or said metal ion reducing system comprises supply passages for introducing pure water and an acid aqueous solution into said system.

4. The waste water treatment apparatus according to any one of claims 1 to 3, wherein:

said electrolytic deposition unit comprises a rotating electrolytic cell having an anode and a rotatable cathode;

said anode is disposed outside said cathode; and

said rotating electrolytic cell is operable to deposit the metal on a surface of said cathode while rotating said cathode.

5. The waste water treatment apparatus according to claim 4, wherein said electrolytic deposition unit further comprises a scraper disposed in contact with or adjacent to said rotatable cathode so that said scraper scrapes off the metal deposited on the surface of said cathode.

6. The waste water treatment apparatus according to claim 5, wherein the metal removed from the surface of said cathode by said scraper is delivered to a filter together with the concentrated water and captured by said filter.

7. The waste water treatment apparatus according to any one of claims 1 to 6, wherein said concentration system and said metal ion reducing system can operate simultaneously.

8. The waste water treatment apparatus according to claim 2, wherein the concentrated water having the lowered concentration of the metal ions is discharged through said discharge passage while said recovery system is operating.

9. The waste water treatment apparatus according to any one of claims 1 to 8, wherein the waste water containing the metal ions is produced in a semiconductor fabrication apparatus or pretreated after being produced in a semiconductor fabrication apparatus.

10. The waste water treatment apparatus according to any one of claims 1 to 9, wherein the metal ions contained in the waste water are copper ions produced in a semiconductor fabrication apparatus for forming copper interconnects.

11. A waste water treatment method for treating waste water having at least metal ions and coexistent cations to produce treated water having a lowered concentration of the metal ions and to recover the metal ions as metal, said method comprising:

a metal ion separation and concentration process for separating the metal ions and the coexistent cations from waste water by electrodialysis operation in a metal ion separation and concentration unit to produce treated water having lowered concentrations of the metal ions and the coexistent cations and to produce concentrated water having increased concentrations of the metal ions and the coexistent cations;

a concentration process for circulating and supplying the concentrated water to said metal ion separation and concentration unit to produce concentrated water having further increased concentrations of the metal ions and the coexistent cations;

a recovery process in which an electrolytic deposition unit receives the concentrated water having the further increased concentrations of the metal ions and the coexistent cations to selectively recover the metal ions, and the concentrated water having a lowered concentration of the metal ions is circulated and supplied to said metal ion separation and concentration unit; and

a metal ion reducing process for circulating and supplying the concentrated water having the increased concentration of the coexistent cations to said electrolytic deposition unit to produce concentrated water having a lowered concentration of the metal ions.

12. The waste water treatment method according to claim 11, further comprising a discharge process in which the concentrated water having the lowered concentration of the metal ions produced by said metal ion reducing process is discharged out of a system in which said waste water treatment method is carried out.

13. The waste water treatment method according to claim 12, further comprising a replenishment process for replenishing the system with pure water and an acid aqueous solution after said discharge process.

14. The waste water treatment method according to any one of claims 11 to 13, wherein:

said electrolytic deposition unit comprises a rotating electrolytic cell having an anode and a rotatable cathode;

said anode is disposed outside said cathode; and

said rotating electrolytic cell is operable to deposit the metal on a surface of said cathode while rotating said cathode.

15. The waste water treatment method according to claim 14, wherein the metal deposited on the surface of said cathode is scraped off by a scraper disposed in contact with or adjacent to said rotatable cathode.

16. The waste water treatment method according to claim 15, wherein the metal removed from the surface of the cathode by the scraper is delivered to a filter together with the concentrated water and captured by the filter.

17. The waste water treatment method according to any one of claims 11 to 16, wherein said concentration process and said metal ion reducing process can be performed simultaneously.

18. The waste water treatment method according to any one of claims 12 to 17, wherein said discharge process is performed during said recovery process to discharge the concentrated water having the lowered concentration of the metal ions.

19. The waste water treatment method according to any one of claims 11 to 18, wherein the waste water containing the metal ions is produced in a semiconductor fabrication apparatus or pretreated after being produced in a semiconductor fabrication apparatus.

20. The waste water treatment method according to any one of claims 11 to 19, wherein the metal ions contained in the waste water are copper ions produced in a semiconductor fabrication apparatus for forming copper interconnects.

FIG. 1A

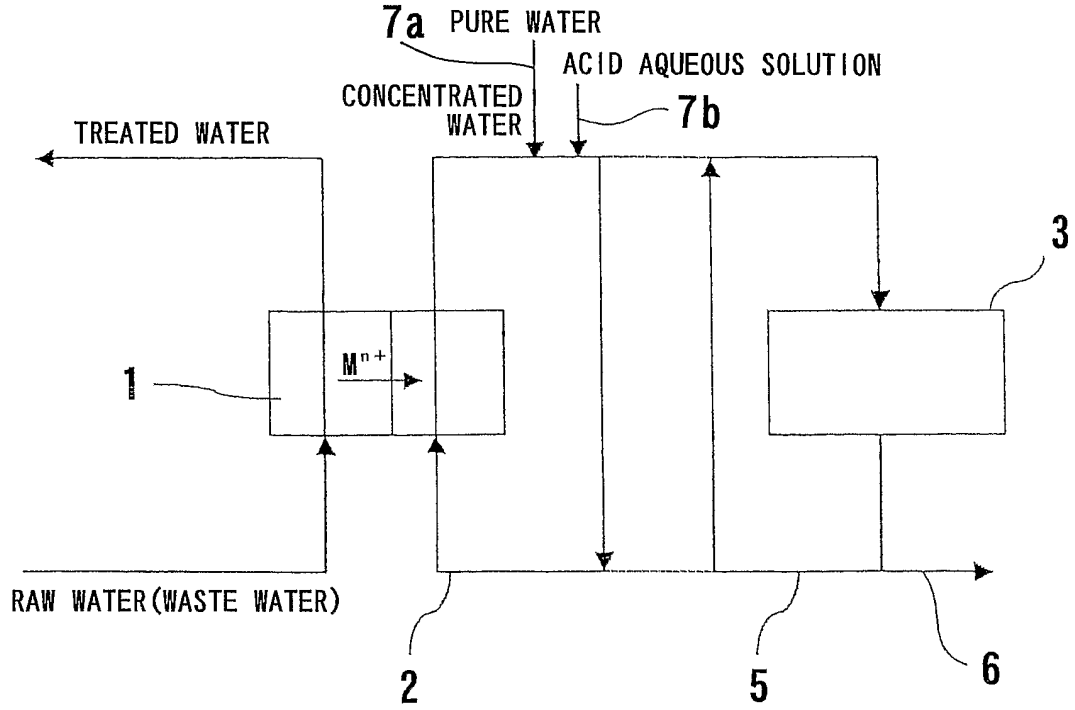

7a PURE WATER
ACID AQUEOUS SOLUTION
CONCENTRATED WATER
7b
TREATED WATER
3
1
M^{n+}
RAW WATER(WASTE WATER)
2
5
6

FIG. 1B

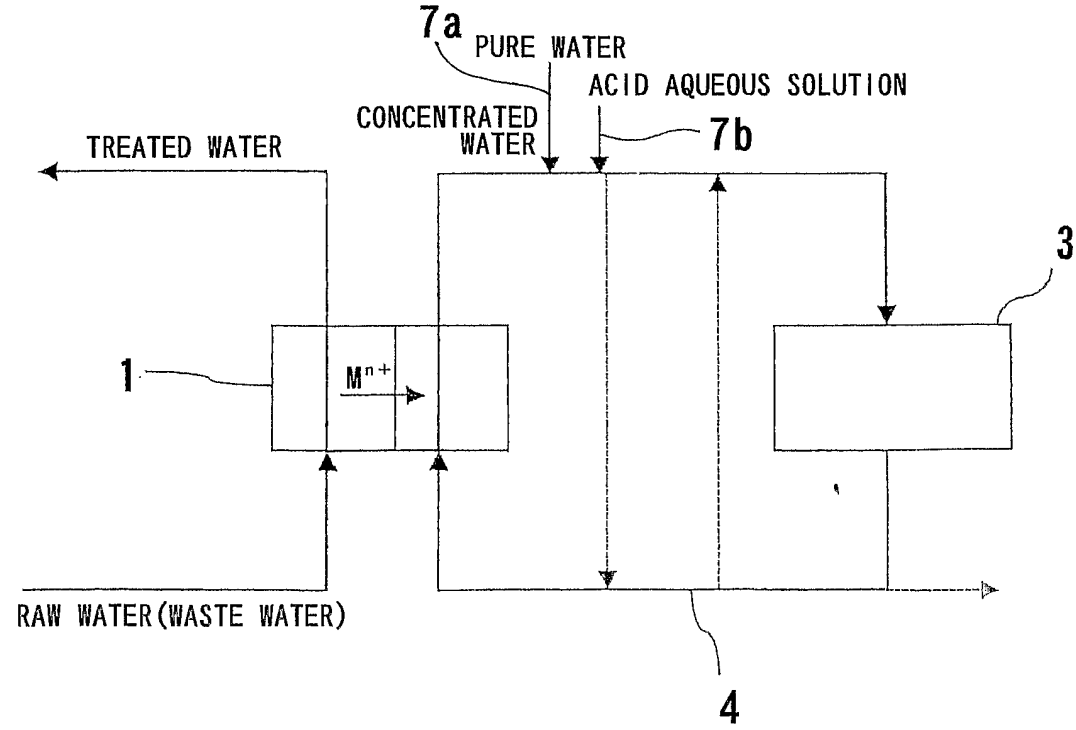
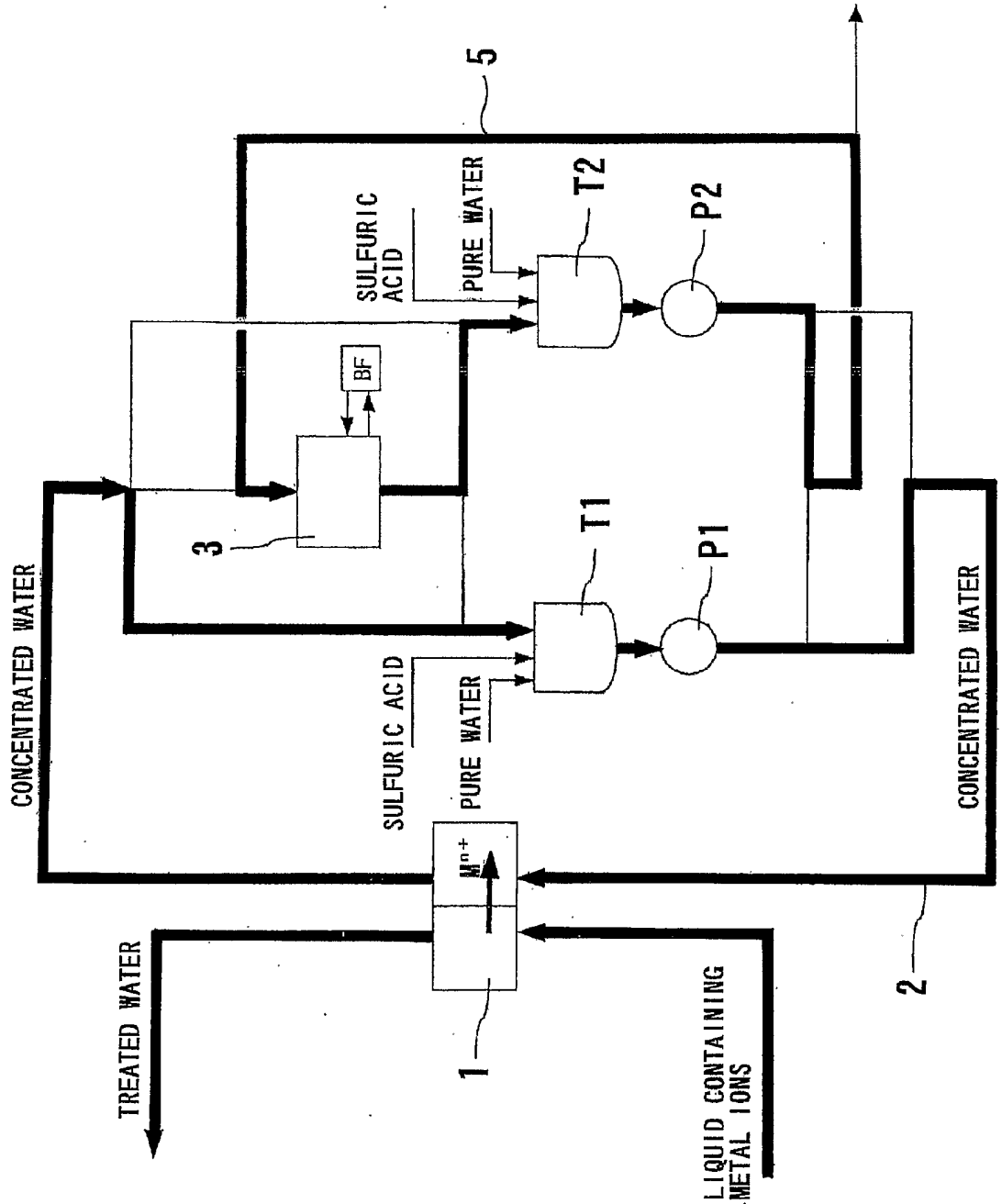

7a PURE WATER
ACID AQUEOUS SOLUTION
CONCENTRATED WATER
7b
TREATED WATER
3
1
M^{n+}
RAW WATER(WASTE WATER)
4

FIG. 2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PURE WATER
T2
P2
BF
3
T1
P1
CONCENTRATED WATER
SULFURIC ACID
PURE WATER
CONCENTRATED WATER
M^{n+}
TREATED WATER
1
LIQUID CONTAINING METAL IONS
2

FIG. 3

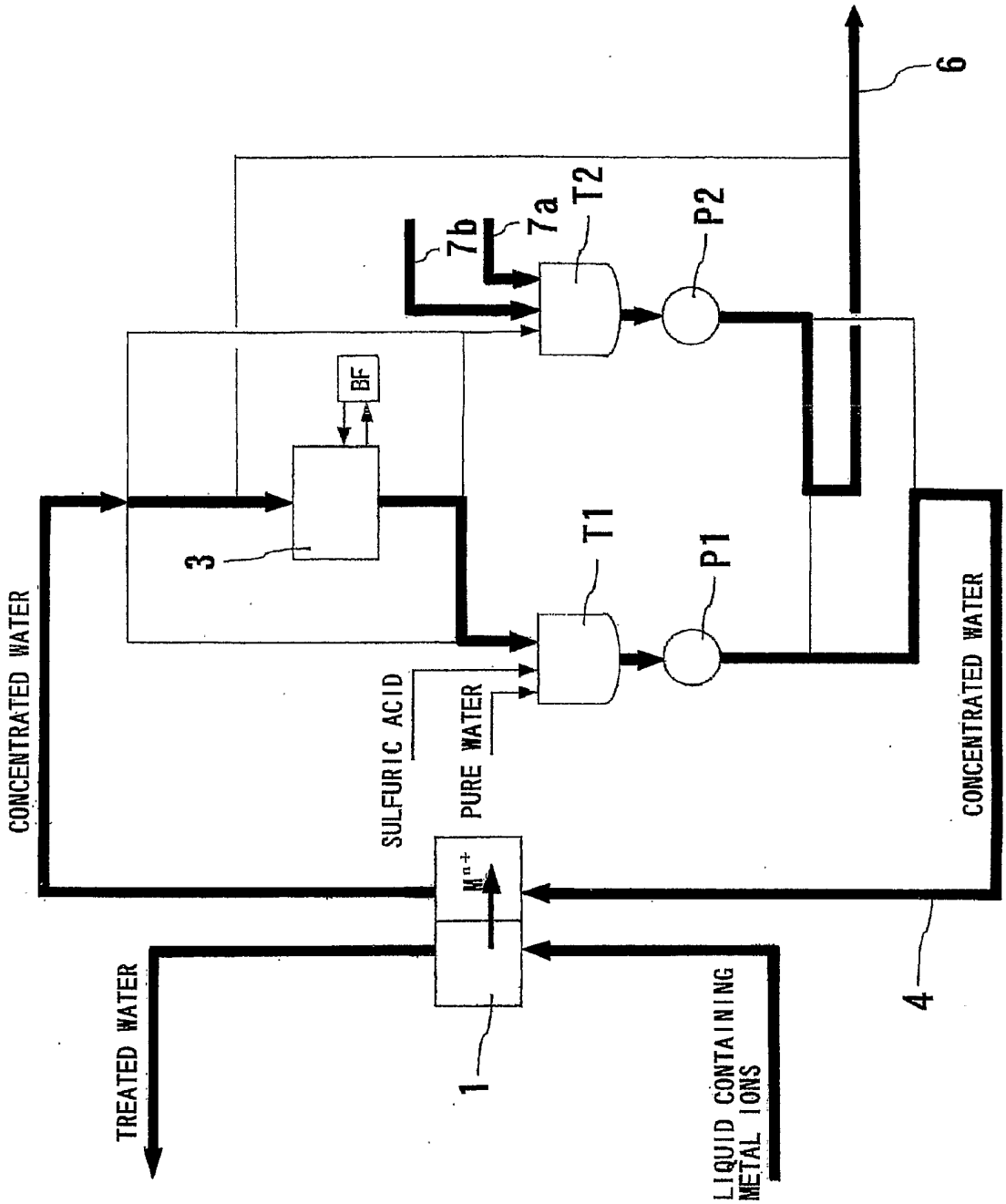
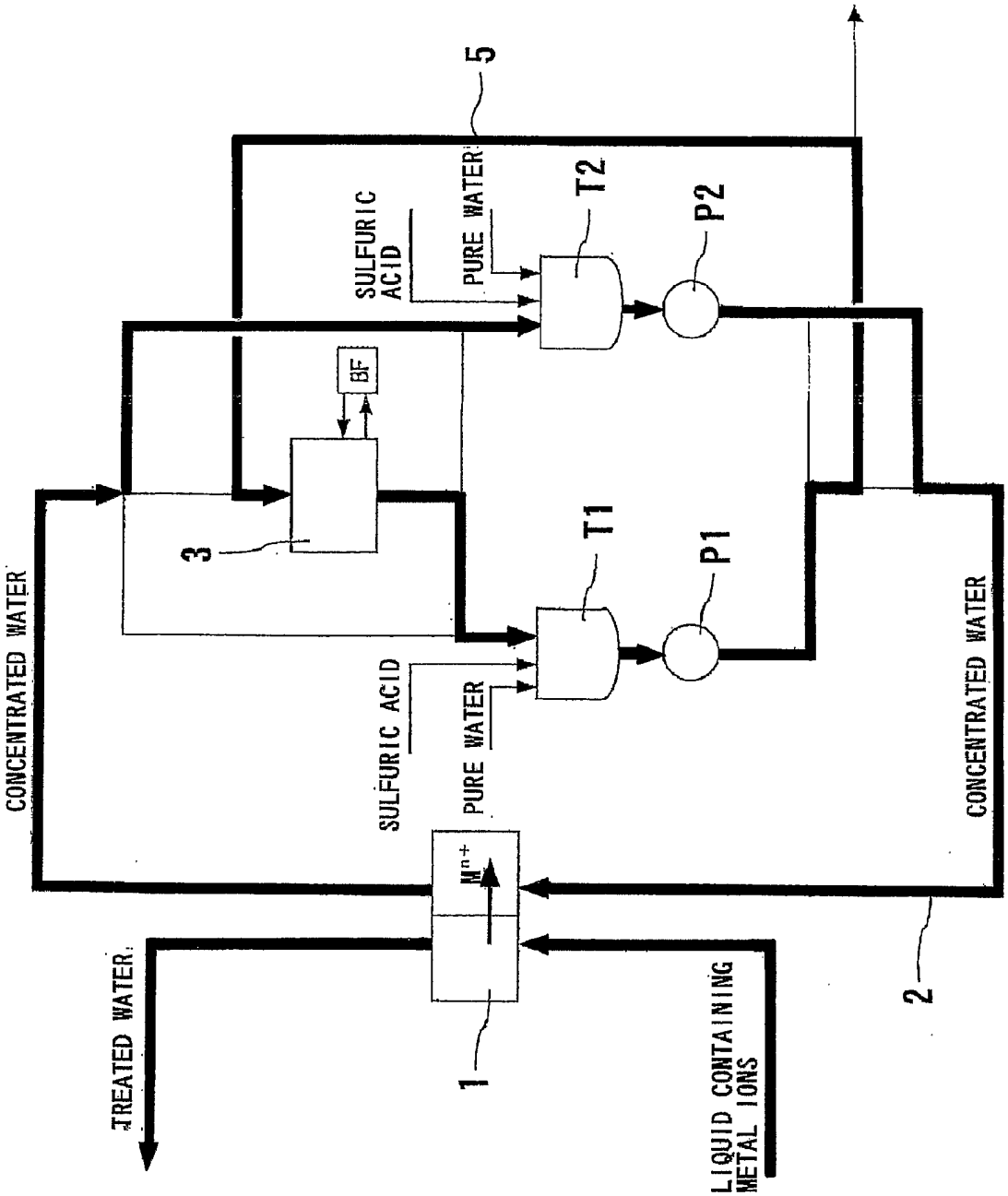

6
7b
7a
T2
P2
BF
3
T1
P1
CONCENTRATED WATER
SULFURIC ACID
PURE WATER
CONCENTRATED WATER
M^{n+}
TREATED WATER
1
LIQUID CONTAINING METAL IONS
4

FIG. 4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PURE WATER
SULFURIC ACID
T2
P2
BF
3
T1
P1
CONCENTRATED WATER
SULFURIC ACID
PURE WATER
M^{n+}
CONCENTRATED WATER
TREATED WATER
1
2
LIQUID CONTAINING METAL IONS

FIG. 5

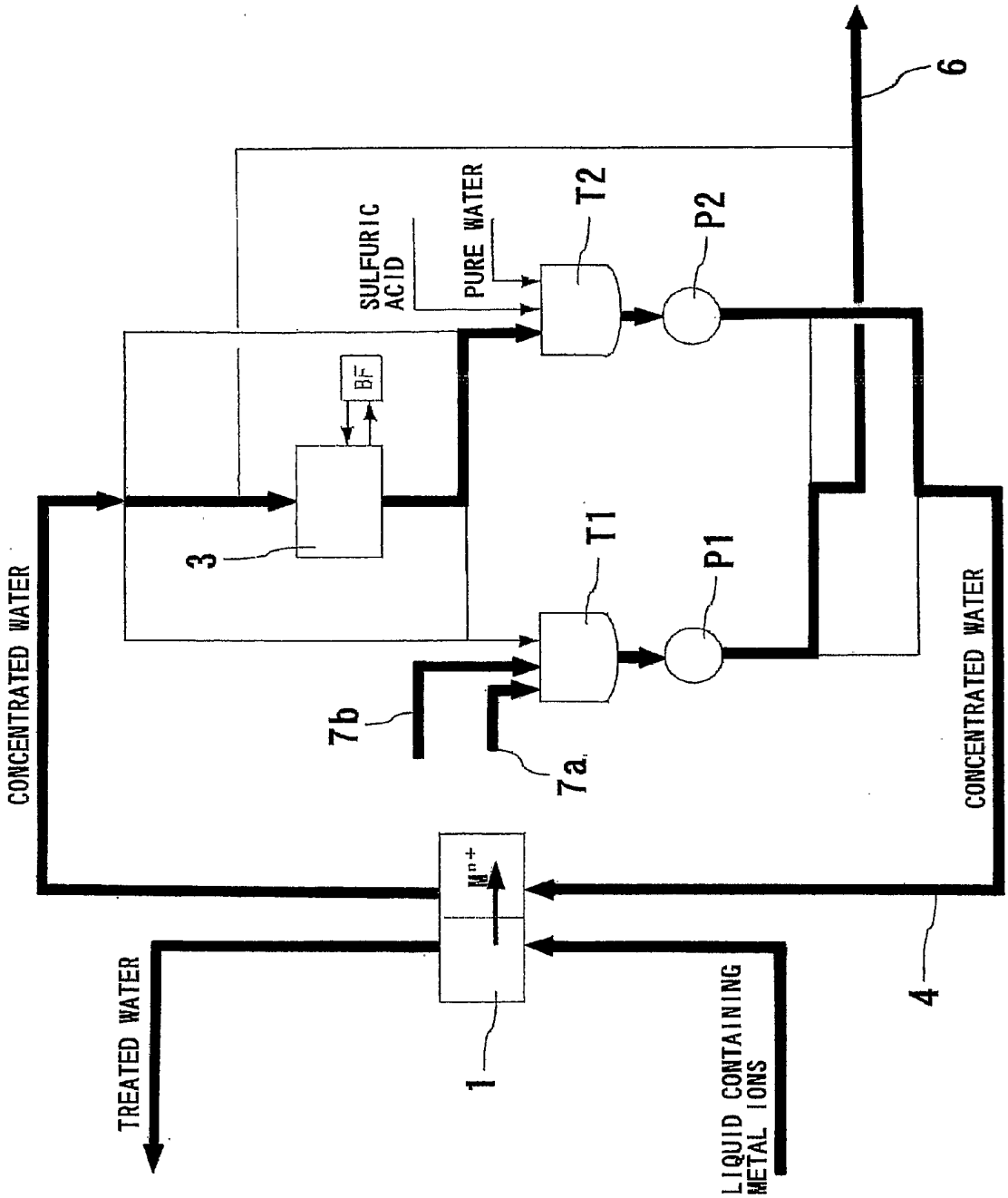

CONCENTRATED WATER
TREATED WATER
LIQUID CONTAINING METAL IONS
CONCENTRATED WATER
SULFURIC ACID
PURE WATER
BF
T1
T2
P1
P2
1
3
4
6
7a
7b

FIG. 6

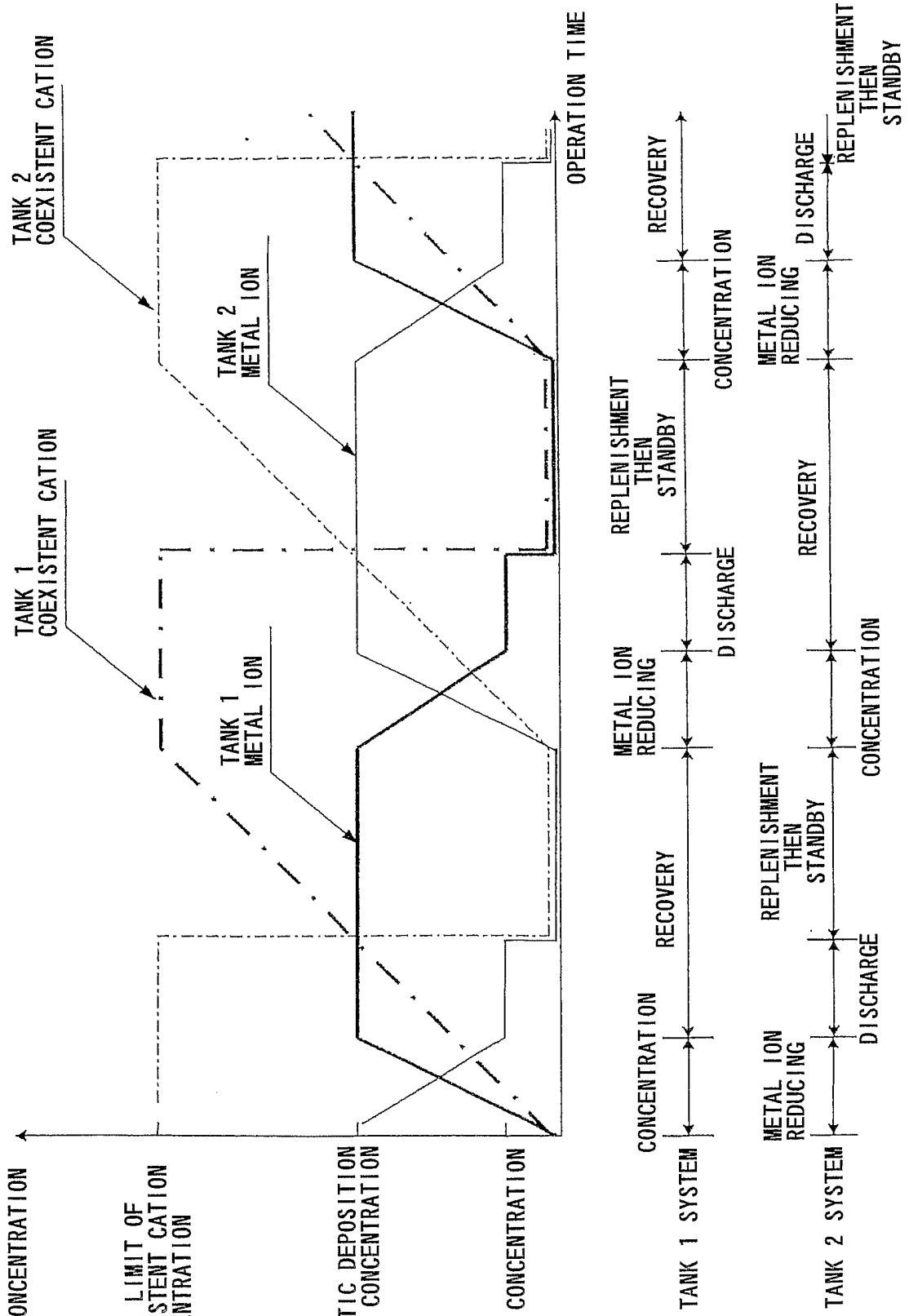

ION CONCENTRATION
UPPER LIMIT OF COEXISTENT CATION CONCENTRATION
ELECTROLYTIC DEPOSITION METAL ION CONCENTRATION
DISCHARGE METAL ION CONCENTRATION
OPERATION TIME
TANK 1 COEXISTENT CATION
TANK 2 COEXISTENT CATION
TANK 1 METAL ION
TANK 2 METAL ION
TANK 1 SYSTEM
CONCENTRATION
RECOVERY
METAL ION REDUCING
REPLENISHMENT THEN STANDBY
DISCHARGE
TANK 2 SYSTEM
CONCENTRATION
RECOVERY
METAL ION REDUCING
REPLENISHMENT THEN STANDBY
DISCHARGE

FIG. 7

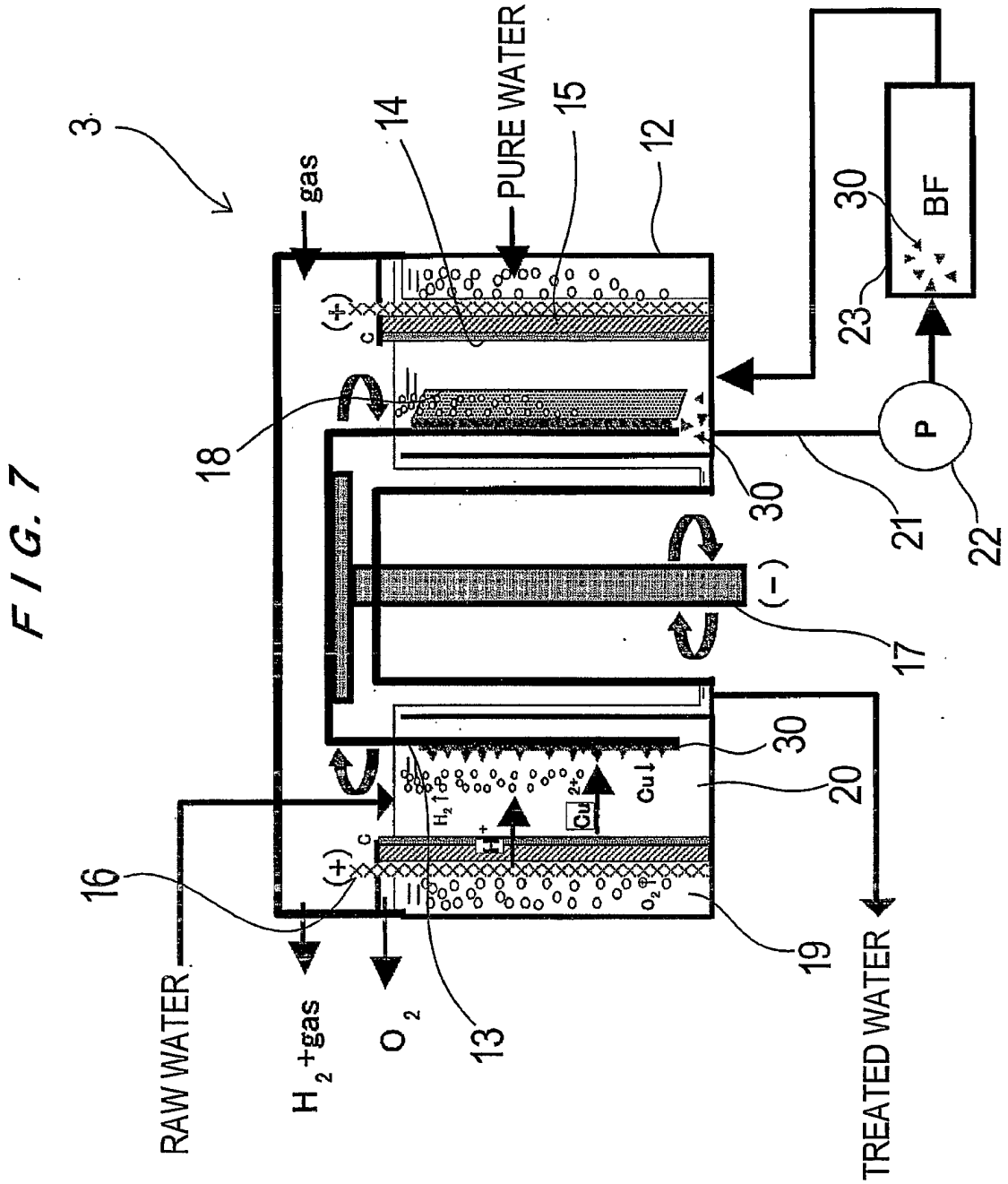

3
gas
14
PURE WATER
15
12
30
BF
23
(+)
C
18
30
P
21
22
(-)
17
30
20
Cu
H_2
Cu^{2+}
H^+
16
(+)
C
O_2
19
RAW WATER
H_2+gas
O_2
13
TREATED WATER

FIG. 8

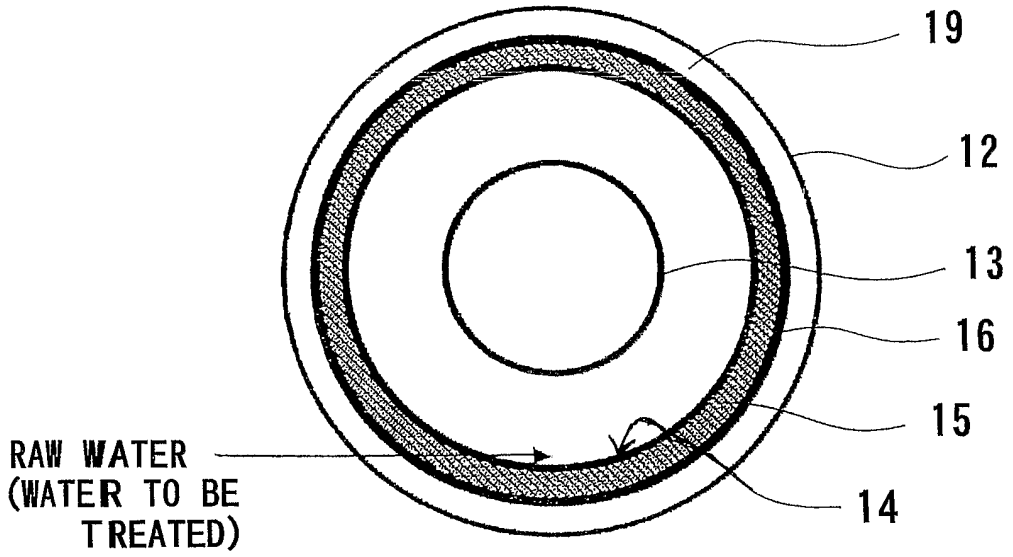


FIG. 9

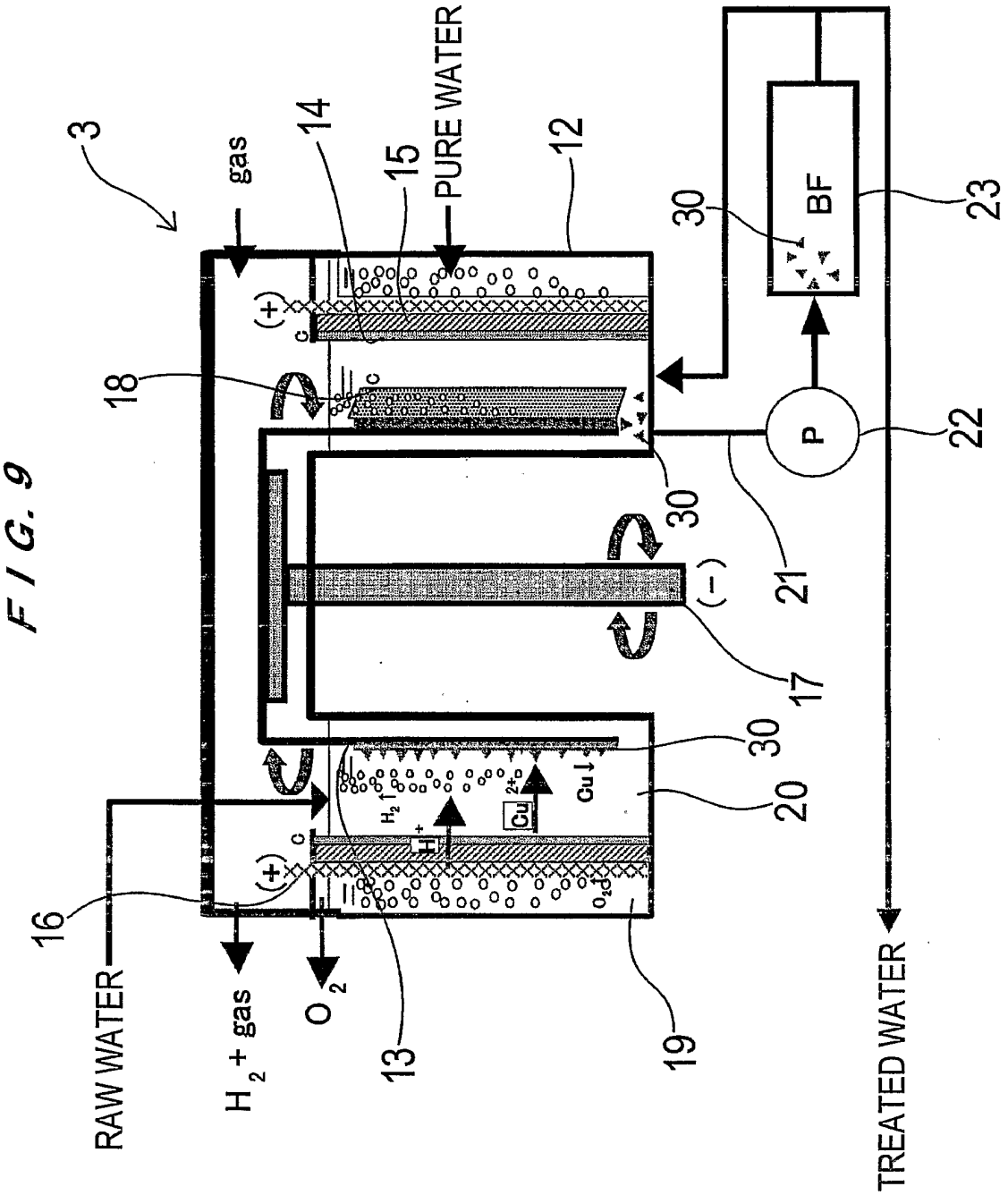

3
gas
14
15
PURE WATER
12
30
BF
23
18
(+)
C
P
22
30
21
(−)
17
30
20
Cu
Cu
$H_2\uparrow$
H^+
16
(+)
C
O_2
RAW WATER
H_2 + gas
O_2
13
19
TREATED WATER

FIG. 10

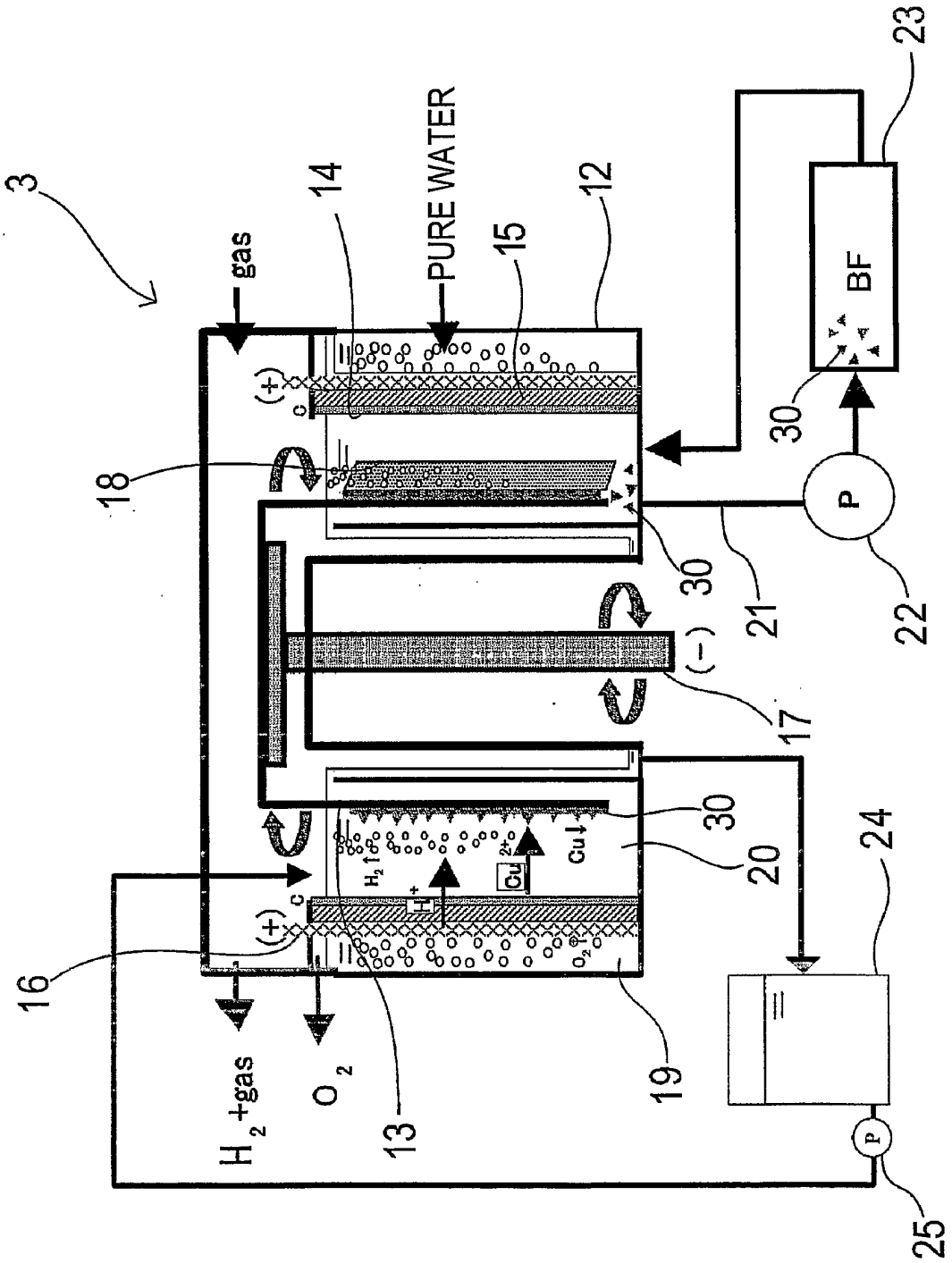

3
gas
14
PURE WATER
15
12
23
BF
30
18
(+)
C
P
30
21
22
(−)
17
30
20
24
Cu
Cu
16
(+)
C
19
H_2+gas
O_2
13
25

FIG. 11

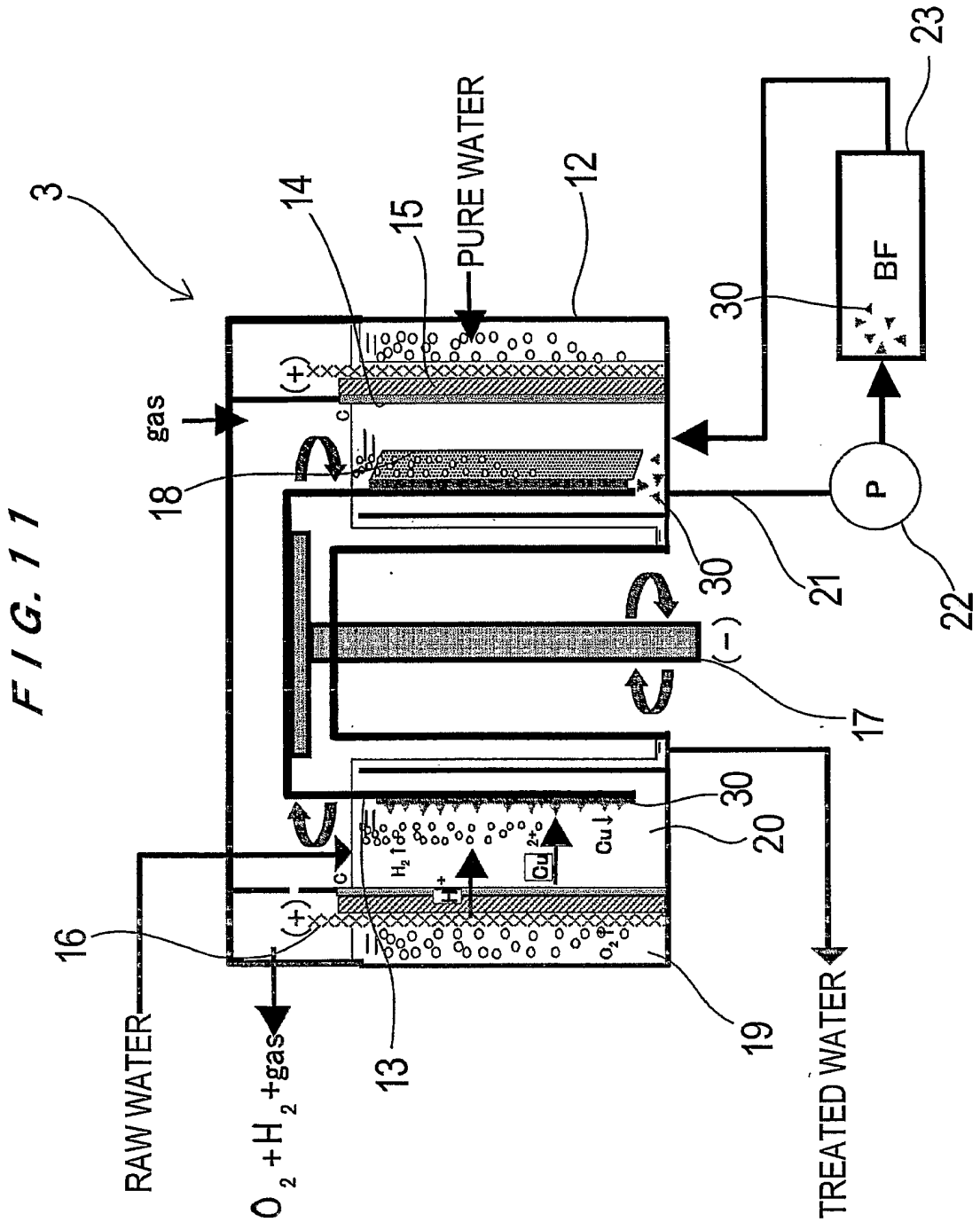

3
14
15
PURE WATER
12
23
BF
30
gas
18
(+)
C
30
21
P
22
(−)
17
30
20
Cu
Cu
16
(+)
C
13
19
RAW WATER
O2+H2+gas
TREATED WATER

FIG. 12A

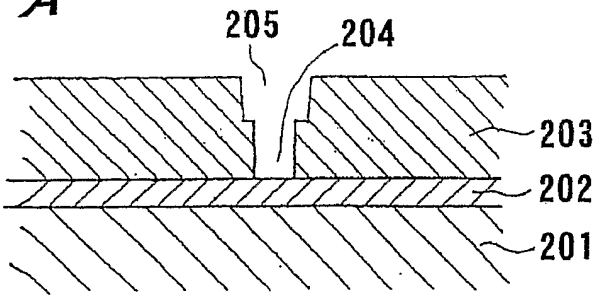


FIG. 12B

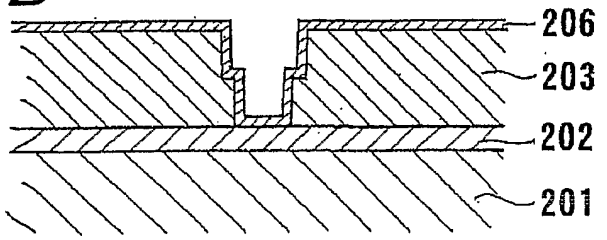


FIG. 12C

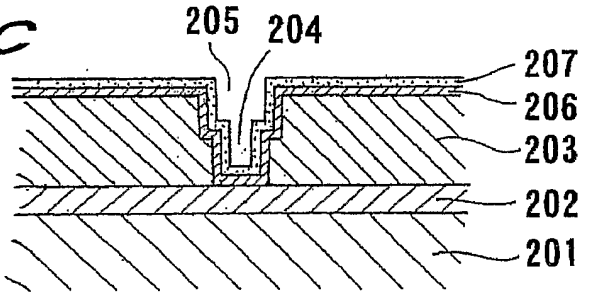


FIG. 12D

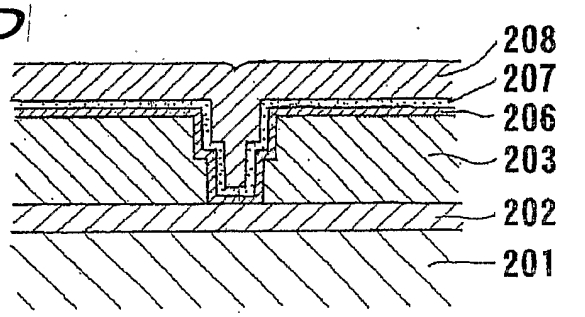
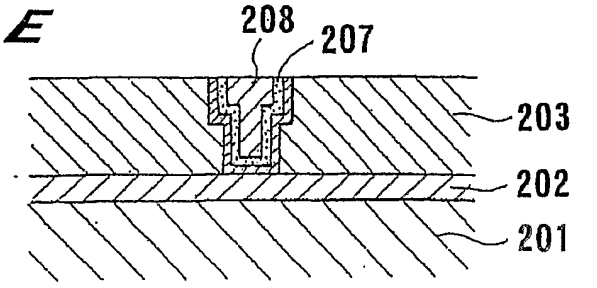


FIG. 12E



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/018387

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. *C02F1/461* (2006.01), *C02F1/469* (2006.01), *B01D61/44* (2006.01), *C22B3/42* (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. C02F1/461 , C02F1/469 , B01D61/44 , C22B3/42

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

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2006
Registered utility model specifications of Japan 1996-2006
Published registered utility model applications of Japan 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-001346 A (TOSHIBAPURANTOKENSETU KK.) 2002.01.08, Claims1-3, Fig1 (Family:none)	1-20
A	JP 52-101690 A (ASAHIGARASU KK.) 1977.08.25, Claim1, Figs1-3 (Family:none)	1-20
E, A	JP 2006-000792 A (KK. EBARASEISAKUSYO) 2006.01.05, Claims1-19, Figs1-6 (Family:none)	1-20
A	JP 61-106788 A (TOPPANINSATU KK.) 1986.05.24, Claim1, Fig2 (Family:none)	1-20

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
04.01.2006	17.01.2006

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