

{DESCRIPTION}

{Title of Invention}

CHEMICAL CLEANING METHOD AND CHEMICAL CLEANING DEVICE

{Technical Field}

{0001}

The present invention relates to a chemical cleaning method and a chemical cleaning device for removing hematite adhering to an inner surface of a water wall tube and the like.

{Background Art}

{0002}

A thermal power generation system 1 exemplarily illustrated in Fig. 20 includes a once-through boiler 10. As a water supply system of a boiler, condenser 20, a demineralizer 21, a gland steam condenser 22, a low-pressure water supply heater 23, a deaerator 24, a high-pressure water supply heater 25, and an economizer 26 are installed. As a steam system of the boiler, a steam-water separator 30, a superheater 31, a turbine 32, and a reheater 33 are installed. As the turbine 32, a high-pressure turbine, a low-pressure turbine, and a low-pressure turbine may be installed.

{0003}

In the thermal power generation system 1 in which oxygen treatment is applied to the boiler water supply system, a phenomenon of a rise of a metal temperature of a water wall

tube of the once-through boiler 10 occurs, and occurrence of leakage of boiler water supply due to breakage of the water wall tube becomes problem. A cause of the rise of the metal temperature of the water wall tube is that iron is eluted from piping of a low-pressure water supply heater drain system 27 or the water supply system and hematite (Fe_2O_3) is generated and hematite adheres to/deposited on an inner surface of the water wall tube, and thermal conductivity is deteriorated.

{0004}

To prevent the improper leakage of the water wall tube, periodic chemical cleaning of the water wall tube is conducted and removal of scale made of iron-based oxides such as hematite deposited on the surface of the tube is performed. In conventional chemical cleaning, washing inside the water wall tube is conducted such that a circuit is installed between the economizer 26 to the steam-water separator 30, and an acid washing liquid (a hydrochloric acid or the like) heated to about 60 °C to 80°C is brought to circulate in the circuit (for example, see PTL 1).

{0005}

PTL 2 discloses a method of removing sludge and the like generated in a reactor steam generator. PTL 3 discloses a method of washing and removing iron oxide scale from a filter made of metal used in thermal power generation plants or atomic power generation plants. In the method of PTL 3, the

iron oxide scale is separated from the filter, by dissolving only iron of an adhering portion, of iron oxide adhering to the filter.

{Citation List}

{Patent Literature}

{0006}

{PTL 1} Japanese Unexamined Patent Application, Publication No. H8-105602

{PTL 2} Japanese Translation of PCT International Application, Publication No. 2004-535546

{PTL 3} Japanese Unexamined Patent Application, Publication No. 2013-71111

{Summary of Invention}

{Technical Problem}

{0007}

In the conventional chemical cleaning like PTL 1, the installed circuit needs to be filled with the washing liquid. Further, a hydrogen gas is generated during washing due to use of the acid washing liquid. Therefore, the chemical cleaning cannot be performed in parallel with mechanical/electrical work in which fire is used. As described above, while the chemical cleaning is conducted, maintenance work cannot be performed not only for devices immersed in the washing liquid but also for other devices, and thus there is a problem that maintenance cannot be efficiently performed.

{0008}

In the conventional chemical cleaning method, the washing liquid needs to circulate at a high flow velocity to remove the scale made of iron-based oxide. Further, to obtain a sufficient flow rate, the boiler needs to be connected to piping with a large diameter. However, upstream-side piping and downstream-side piping of the once-through boiler 10 have a small diameter and are inappropriate to be connected with a chemical cleaning device. Therefore, as specifically described in PTL 1, the circuit needs to be connected to upstream-side piping of the economizer 26 and piping in the steam-water separator 30, and thus there is a device constraint.

{0009}

Hematite is a poorly soluble oxide, and is less easily dissolved in the washing liquid in a conventional acid washing liquid (for example, in a hydrochloric acid-based liquid or a citric acid-based liquid), and sludge is generated through the chemical cleaning.

Further, a magnetite layer, which is natural oxide scale, is formed on the piping or the surface of the filter made of metal of PTL 3. In the method of PTL 3, the scale is separated by dissolving only the magnetite layer without dissolving all of adhering iron oxide scale. Therefore, if the method disclosed in PTL 3 is used, sludge is generated.

{0010}

Since the piping of the water wall tube and the like of the once-through boiler 10 in the thermal power generation system 1 is long and the shape is complicated, sludge is partially integrated in the middle of the piping and may block an inside the piping if the sludge is generated.

Therefore, in the conventional chemical cleaning, the sludge needs to be removed from the washing liquid. Examples of a method of removing sludge include a method of providing a filter in the middle of a portion where the washing liquid passes through and collecting the sludge floating in the washing liquid, and a method of cutting a part of piping and the like of a device to be washed and inspecting an inside of the piping after chemical cleaning, and welding the piping again after removing the sludge by a physical method such as suction cleaning.

{0011}

Further, in the conventional chemical cleaning using an acid washing liquid, the washing liquid needs to be heated, as described above. Therefore, a temperature raising facility for heating the washing liquid needs to be separately installed. Further, the inside of the device immersed in the acid washing liquid needs to be neutralized after washing, and thus a large amount of neutralizing water is required.

{0012}

In a case where there is the superheater 31 including parts made of stainless steel on a downstream side of the steam-water separator 30, like the thermal power generation system illustrated in Fig. 20, if the parts made of stainless steel comes in contact with the acid washing liquid such as a hydrochloric acid, the parts may corrode. Therefore, in the conventional chemical cleaning, immersion of the washing liquid needs to be prevented by filling, with water, a non-washing system adjacent to the downstream side of the device to be washed, and pressurizing the non-washing system, and thus a water filling/pressurizing pump is installed.

{0013}

As described above, when performing the conventional chemical cleaning, a large amount of washing liquid and water for water filling and neutralization are required, and beyond that, a large facility and its installation work are required. Further, a work period spans long periods of time. Therefore, high maintenance cost has been a problem.

{0014}

The present invention has been made in view of the foregoing, and an objective is to provide a chemical cleaning method of removing hematite, and a chemical cleaning device for conducting the chemical cleaning method.

{Solution to Problem}

{0015}

A first aspect of the present invention is a chemical cleaning method including: a washing liquid supply process of supplying a washing liquid containing a rust removing agent that is a chelating agent, a reducing agent, or a mixture of the chelating agent and the reducing agent, to a device to be washed including a member to which hematite adheres; and a washing process of immersing at least a region to which the hematite adheres in the member into the washing liquid, maintaining an oxidation-reduction potential of the washing liquid at a value at which the hematite is eluted into the washing liquid, and removing the hematite from the member, wherein the chelating agent is any one of an aminocarboxylic acid-based chelating agent, an oxycarbonic acid-based chelating agent, and an organic phosphorus-based chelating agent, the reducing agent is any one of a metal ion, sulfite, an oxalic acid, a formic acid, an ascorbic acid, pyrogallol, hydrazine, and hydrogen, and pH of the washing liquid falls within a range of 4 to 8.

{0016}

A second aspect of the present invention is a chemical cleaning device for performing chemical cleaning of a device to be washed including a member to which hematite scale adheres, the chemical cleaning device including: a chemical tank adapted to accommodate a washing liquid containing a rust removing agent that is a chelating agent, a reducing agent, or

a mixture of the chelating agent and the reducing agent, and having pH falling within a range of 4 to 8, the chelating agent being any one of an aminocarboxylic acid-based chelating agent, an oxycarbonic acid-based chelating agent, and an organic phosphorus-based chelating agent, and the reducing agent being any one of a metal ion, sulfite, an oxalic acid, a formic acid, an ascorbic acid, pyrogallol, hydrazine, and hydrogen; a chemical supply line connecting the device to be washed and the chemical tank, and adapted to supply the washing liquid to the member; a pump installed in the chemical supply line; a chemical discharge line connecting the device to be washed and the chemical tank, and adapted to discharge the washing liquid from the member; a means adapted to immerse at least a region to which the hematite adheres in the member into the washing liquid; and a means adapted to maintain an oxidation-reduction potential of the washing liquid during washing at a value at which the hematite is eluted into the washing liquid, wherein the chemical tank, the chemical supply line, and the pump are means to supply the washing liquid to the member.

{0017}

In the chemical cleaning method and the chemical cleaning device of the above aspects, the washing liquid is fed to the device to be washed only. Therefore, an amount of washing liquid required for the chemical cleaning can be significantly

reduced.

Further, since the washing liquid containing the rust removing agent is used, water filling and the like for preventing corrosion of the member are not necessary even if a device including parts made of stainless steel is arranged on a downstream-side of the device to be washed. A facility for the water filling is unnecessary, and the device configuration becomes simplified. Further, since hydrogen is not generated in washing, the chemical cleaning can be conducted in parallel with mechanical work or electrical work using fire, and inspection and maintenance work of units can be conducted in parallel. Therefore, a maintenance work period can be shortened.

As described above, by use of the chemical cleaning method and the chemical cleaning device of the present invention, cost required for maintenance such as facility cost and chemical cost can be significantly reduced.

{0018}

In the chemical cleaning method, the value is maintained within a range from -0.8 V to -0.4 V , both inclusive, on a basis of a silver-silver chloride electrode reference, and the washing process is conducted.

In the chemical cleaning method, the value may be adjusted by supplying a reducing atmosphere gas to the device to be washed.

{0019}

The chemical cleaning device further includes a reducing atmosphere adjustment unit adapted to adjust the oxidation-reduction potential of the washing liquid during washing to a value within a range from -0.8 V to -0.4 V, both inclusive, on a basis of a silver-silver chloride electrode reference.

In the chemical cleaning device, the reducing atmosphere adjustment unit may supply a reducing atmosphere gas to the equipment to be washed.

{0020}

By maintaining a reduced state as the oxidation-reduction potential, hematite is dissolved in the washing liquid and is removed. Few solids such as sludge are generated by washing, and even if a few solids are generated, the solids can be easily discharged from the device to be washed together with the washing liquid. Further, a facility to remove the sludge is unnecessary. Therefore, facility cost can be reduced.

{0021}

In the chemical cleaning method, a temperature of the washing liquid during the washing process preferably falls within a range from an environmental temperature around the member to a temperature higher than the environmental temperature by 10°C, both inclusive.

{0022}

In the chemical cleaning device, a temperature of the

washing liquid supplied to the member preferably falls within a range from an environmental temperature around the member to a temperature higher than the environmental temperature by 10°C, both inclusive.

Preferably, the chemical cleaning device further includes a circulation loop connecting the chemical supply line on an upstream side and the chemical supply line on a downstream side across the pump, and a part of the washing liquid having passed through the pump is conveyed to the upstream side of the pump through the circulation loop.

{0023}

According to the present invention, removal of hematite is possible at a lower temperature than a case of using an acid washing liquid, and it is not necessary to raise the temperature of the washing liquid in a positive manner, and maintenance of the temperature that is the environmental temperature is extremely easy.

If the temperature of the washing liquid is raised to the temperature higher than the environmental temperature by 10°C, or less, detergency can be further enhanced. For example, the temperature of the washing liquid can be easily raised using heat generated at the time of operation of the pump. The configuration of the present invention does not include cooling in a positive manner, and thus the temperature of the washing liquid can be maintained to be higher than the

environmental temperature for a long time.

According to the present invention, the washing can be conducted at a lower temperature than a conventional method using an acid washing liquid. As a result, facility cost and washing cost can be reduced.

{0024}

In the chemical cleaning method, the region is immersed in the washing liquid in a state where the washing liquid is left to stand.

In the chemical cleaning device, supply of the washing liquid to the member and discharge of the washing liquid from the member are stopped, and the washing liquid is left to stand, during washing.

According to the chemical cleaning method and the chemical cleaning device, installation of a large circuit for the washing liquid and the like is unnecessary, and the washing is conducted with a simple process. Therefore, this is favorable.

{0025}

In the chemical cleaning method, a water supply process is further included between the washing liquid feeding process and the washing process, a predetermined amount of the washing liquid is supplied to the device to be washed in the washing liquid supply process, a predetermined amount of water is supplied to the device to be washed in the water supply

process, and the region is immersed in the washing liquid.

The chemical cleaning device further includes a water supply unit that includes: a water tank adapted to accommodate water; a water supply line connecting the water tank and the device to be washed; and a water filling pump installed in the water supply line.

{0026}

According to the chemical cleaning method and the chemical cleaning device, a layer of the washing liquid and a layer of water can be made separated in the device to be washed. If the region to which hematite adheres is made immersed in the washing liquid, and other portions are made immersed in the water, the amount of washing liquid to be used for the chemical cleaning can be significantly reduced.

{0027}

In the chemical cleaning method, the washing liquid may be accommodated in capsules made of water-soluble polymer, and the capsules may be supplied to the device to be washed.

{0028}

In the chemical cleaning device, the washing liquid may be accommodated in capsules made of water-soluble polymer, the chemical tank may accommodate the capsule, and the capsules may be supplied from the washing liquid tank to the device to be washed.

{0029}

With the chemical cleaning method and the chemical cleaning device, for example, the region in which a large amount of hematite is especially generated can be easily immersed in the washing liquid. Therefore, the amount of use of the washing liquid can be significantly reduced.

{0030}

In the chemical cleaning method, a process of discharging the washing liquid from the member and a process of feeding the discharged washing liquid to the member are repeated, and a height of a liquid level of the washing liquid is moved near the region, during the washing process.

{0031}

In the chemical cleaning device, discharge of the washing liquid in the member toward the chemical tank through the chemical discharge line, and feed of the washing liquid in the chemical tank to the member through the chemical supply line are repeated during washing.

{0032}

According to the chemical cleaning method and the chemical cleaning device, a flow velocity is given to the washing liquid in the region to which hematite adheres, and the washing liquid is stirred. Therefore, detergency is improved and thus this is favorable.

{0033}

In the chemical cleaning method, the washing liquid

passes through the member and is discharged from an upstream-side end portion of the member, and the discharged washing liquid is directly circulated into a downstream-side end portion of the member, during the washing process.

{0034}

The chemical cleaning device further includes a circulation unit including a circulation line connecting an upstream-side end portion and a downstream-side end portion of the member, and a circulation pump installed in the circulation line, and the washing liquid discharged from the downstream-side end portion is circulated to the upstream-side end portion through the circulation line during washing.

{0035}

With the chemical cleaning method and the chemical cleaning device, a flow velocity is given to the washing liquid in the region to which hematite adheres, and the washing liquid is stirred. Therefore, detergency is improved. Further, the washing liquid is warmed in passing through the pump, and the washing is conducted at a higher temperature than the environmental temperature around the member. Therefore, the detergency is improved.

{0036}

The chemical cleaning method according to the first aspect further includes: a measurement process of measuring iron concentration in the washing liquid; and a determination

process of determining a removal state of the hematite from the member on a basis of the iron concentration, and the washing liquid is discharged from the device to be washed during the washing process, and the iron concentration in the discharged washing liquid discharged in the measurement process is measured, and, when the iron concentration is determined to be predetermined concentration or more, or when an amount of change of concentration gradient is determined to be a value within a predetermined range, in the determination process, the washing process is terminated.

{0037}

The chemical cleaning device according to the second aspect further includes a determination unit adapted to determine a removal state in which the hematite from the member is eluted on a basis of iron concentration in the washing liquid discharged from the device to be washed, while an oxidation-reduction potential of the washing liquid of the device to be washed is maintained at a value at which the hematite is eluted into the washing liquid, and the device to be washed is being washed, and adapted to terminate the washing of the device to be washed when the determination unit determines that the iron concentration is predetermined concentration or more, or when the determination unit determines that an amount of change of concentration gradient is a value within a predetermined range.

{0038}

In a case where hematite adheres in the member in an uneven distributed manner, distribution occurs in the iron concentration in the washing liquid while the member is immersed in the washing liquid. Because of the structure of the device to be washed, it is extremely difficult to collect the washing liquid from only near the region to which the hematite adheres in the member in order to measure the iron concentration.

Therefore, in the chemical cleaning method and the chemical cleaning device of the above aspects, termination of the chemical cleaning is determined using the iron concentration in the washing liquid once discharged from the device to be washed during washing. In doing so, not only the measurement of the iron concentration becomes easy, but also the washing liquid is stirred by being discharged from the device to be washed and the iron concentration becomes uniform. Therefore, measurement accuracy is improved. According to the present invention, hematite can be more reliably removed by the chemical cleaning, and an effect to improve maintenance efficiency can be obtained.

{0039}

In the chemical cleaning method, the washing liquid is discharged from the device to be washed at predetermined periods in the washing process, and when the iron

concentration is determined to be less than the predetermined concentration, or when the amount of change of the concentration gradient is determined to be a larger value falling outside the predetermined range, in the determination process, the washing liquid may be returned to the device to be washed.

{0040}

In the chemical cleaning device, the determination unit may determine the removal state of the hematite, using the iron concentration in the washing liquid discharged from the device to be washed and stored in the chemical tank.

{0041}

According to the above aspects, washing of the device to be washed and stirring of the washing liquid can be conducted with the simple process and device configuration.

{0042}

In the chemical cleaning method according to the first aspect, during the washing process, the washing liquid may pass through the member and be discharged from the one end-side end portion of the member, the discharge washing liquid may be directly circulated to the other end-side end portion of the member, and the iron concentration may be measured using a part of the discharged washing liquid in the measurement process.

{0043}

In the chemical cleaning device according to the second aspect, a circulation unit including a circulation line directly connecting one end-side end portion and the other end-side end portion of the member, and a circulation pump installed in the circulation line may be included, the washing liquid discharged from the one end-side end portion may be circulated to the other flow-side end portion through the circulation line during washing, a pick-out portion may be installed in the circulation line, and the determination unit may determine the removal state of the hematite, using the iron concentration in the washing liquid collected through the pick-out portion.

{0044}

In the chemical cleaning method and the chemical cleaning device, a flow velocity is given to the washing liquid in the region to which hematite adheres, and the washing liquid is stirred. Therefore, the detergency is improved. Further, a part of the circulated washing liquid can be used for determination of termination of the chemical cleaning.

{0045}

In the chemical cleaning method according to the first aspect of the present invention, during the washing process, an observation process of observing the color of a surface to which the hematite adheres, and a determination process of determining the removal state of the hematite from the member

on the basis of the color are further included, the surface to which the hematite adheres is the region, or a portion to which the hematite adheres in a test body immersed in the washing liquid, and the washing process is terminated when the color derived from the hematite is determined not to be observed in the determination process.

{0046}

In the chemical cleaning device according to the second aspect of the present invention, a determination unit that determines a removal state in which the hematite is eluted on a surface to which the hematite adheres by observation of a color, and terminates washing of the device to be washed when determining that the color derived from the hematite is not observed, while an oxidation-reduction potential of the washing liquid of the device to be washed is maintained at a value at which the hematite is eluted into the washing liquid and the device to be washed is washing, is further included, and the surface to which the hematite adheres is the region, or a portion to which the hematite adheres, of a test body immersed in the washing liquid.

{0047}

In the chemical cleaning method and the chemical cleaning device of the present aspect, the amount of washing liquid required for the chemical cleaning can be significantly reduced, and a maintenance work period can be shortened.

Therefore, significant reduction of maintenance cost can be realized.

Further, according to the present aspects, termination of the chemical cleaning can be determined by a simple method of determining existence/non-existence of a residual amount of adhering hematite. Therefore, an effect to improve work efficiency is exhibited.

{0048}

In the chemical cleaning method according to the first aspect of the present invention, during the washing process, a measurement process of conducting an ultrasonic measurement or an alternating current characteristic measurement on a surface of the member at an opposite side to the side where the region is formed, and a determination process of determining a removal state of the hematite from the member on the basis of temporal change of measured value obtained in the measurement process are further included, and the washing process is terminated when the measured value is determined to be a predetermined value or less, or when the amount of change of change gradient of the measured value is determined to be a value within a predetermined range, in the determination process.

{0049}

In the chemical cleaning device according to the second aspect of the present invention, a measurement unit installed

on a surface of the member at an opposite side to the surface where the hematite is formed, and which conducts ultrasonic measurement or alternating current characteristic measurement for the member, and a determination unit that determines a removal state of the hematite from the member on the basis of temporal change of measured value acquired by the measurement unit, and terminates washing of the device to be washed when determining that the measured value is a predetermined value or less, or when determining that the amount of change of change gradient of the measured value is a value within a predetermined range, while an oxidation-reduction potential of the washing liquid of the device to be washed is maintained at a value at which the hematite is eluted into the washing liquid and the device to be washed is washing, are further included.

{0050}

In the chemical cleaning method and the chemical cleaning device, the measured value is favorably the thickness of the hematite adhering to the member, which can be obtained in the ultrasonic measurement.

{0051}

Alternatively, in the chemical cleaning method and the chemical cleaning device, the measured value is favorably reactance obtained in the alternating current characteristic measurement.

{0052}

In the chemical cleaning method and the chemical cleaning device of the present aspects, the amount of the washing liquid required for the chemical cleaning can be significantly reduced, and the maintenance work period can be shortened. Therefore, significant reduction of the maintenance cost can be realized.

Further, the present aspects have focused on the fact that the measured value acquired through the ultrasonic measurement or the alternating current characteristic measurement from the surface at the opposite side to the hematite adhering surface is changed corresponding to an adhering state of the hematite. The present aspects do not need to collect the washing liquid, and have an advantage of promptly determining termination of the chemical cleaning by a simple method of determining existence/non-existence of a residual amount of the adhering hematite.

{0053}

In the chemical cleaning method according to the first aspect of the present invention, in the washing process, a process of discharging the washing liquid from the member in a state where the oxidation-reduction potential of the washing liquid is maintained at a value at which the hematite is eluted into the washing liquid, and a process of feeding at least a part of the washing liquid to the member are repeated,

the hematite is removed from the member while the height of a liquid level of the washing liquid is moved near the region, a measurement process of measuring a pressure of the washing liquid discharged from the member during the process of discharging, and a determination process of determining a removal state of the hematite from the member on the basis of change of the pressure obtained in the measurement process are performed, the washing liquid is fed to the member while the amount of feed is changed at a predetermined frequency in the process of feeding, and in the determination process, the washing process is terminated, when a phase difference between a waveform of change of the amount of feed of the washing liquid and a waveform of change of the pressure is determined to be a predetermined value or less, when the amount of change of change gradient of the phase difference is determined to be a value within a predetermined range, when a period or amplitude of the waveform of change of the pressure is determined to be a predetermine value or less, or when the amount of change of change gradient of the period or the amount of change of change gradient of the amplitude is determined to be a value within a predetermined range.

{0054}

In the chemical cleaning device according to the second aspect of the present invention, a valve installed at the chemical supply line, a pressure measurement unit installed in

the chemical discharge line, and a determination unit are further included, discharge of at least a part of the washing liquid in the member toward the chemical tank through the chemical discharge line, and feed of the washing liquid in the chemical tank to the member through the chemical supply line are repeated, while an oxidation-reduction potential of the washing liquid of the device to be washed is maintained at a value at which the hematite is eluted into the washing liquid and the device to be washed is washing, the pump or the valve changes the amount of feed of the washing liquid to be fed to the member at a predetermined frequency, the pressure measurement unit measures a pressure of the washing liquid distributed in the chemical discharge line while the device to be washed is being washed, the determination unit determines a removal state of the hematite from the member on the basis of change of the pressure, and the determination unit terminates washing of the device to be washed, when a phase difference between a waveform of change of the amount of feed of the washing liquid and a waveform of change of the pressure is determined to be a predetermined value or less, when the amount of change of change gradient of the phase difference is determined to be a value within a predetermined range, when a period or amplitude of the waveform of change of the pressure is determined to be a predetermine value or less, or when the amount of change of change gradient of the period or the

amount of change of change gradient of the amplitude is determined to be a value within a predetermined range.

{0055}

According to the chemical cleaning method and the chemical cleaning device of the above aspects, the discharge and feed of the washing liquid are repeated, and the liquid level is moved, during the washing process, so that a flow velocity is given to the washing liquid in the region to which hematite adheres, and the washing liquid is stirred.

Therefore, it is favorable because the detergency is improved.

{0056}

A friction coefficient between the washing liquid and the member is changed according to an adhering state of hematite. The inventors of the present invention have found that the liquid level of the washing liquid vibrates in the member when the amount of feed is changed at a predetermined frequency at the time of feeding the washing liquid, and this vibration state is reflected to pressure change of the washing liquid at the time of discharge. According to the present aspects, removal of hematite can be easily determined on the basis of a phase difference between the frequency and the pressure change, and a waveform of the pressure change.

{Advantageous Effects of Invention}

{0057}

According to the present invention, the amount of use of

the washing liquid can be reduced, compared with a conventional chemical cleaning method, and the device configuration of the chemical cleaning device is simplified. Therefore, cost required for chemical cleaning can be significantly reduced.

Further, in the present invention, the washing liquid is not fed to other devices and hydrogen is not generated at the time of washing. Therefore, other work can be performed at the same time with the chemical cleaning. Therefore, the present invention exhibits an advantageous effect to reduce the maintenance work period, compared with conventional technologies.

Further, in the present invention, the removal state of hematite is monitored using a parameter measured during the washing process, and timing to terminate the washing process is determined. Therefore, hematite can be reliably removed from the surface of the member.

{Brief Description of Drawings}

{0058}

{Fig. 1} Fig. 1 is a diagram for describing a chemical cleaning device according to a first embodiment.

{Figs. 2(a) and 2(b)} Figs. 2(a) and 2(b) are schematic views of an example of a once-through boiler.

{Figs. 3(a) and 3(b)} Figs. 3(a) and 3(b) are schematic views of an example of a once-through boiler.

{Fig. 4} Fig. 4 is a schematic view for describing a chemical cleaning method of the first embodiment.

{Fig. 5} Fig. 5 is a SEM photograph of a section surface of a water wall tube before washing liquid immersion.

{Fig. 6} Fig. 6 is a SEM photograph of the section surface of the water wall tube after chemical cleaning.

{Fig. 7} Fig. 7 is a schematic view of a test piece used for washing process termination determination based on color change.

{Fig. 8} Fig. 8 is a diagram for describing a washing process termination determination method based on color change.

{Fig. 9} Fig. 9 is a schematic diagram for describing a chemical cleaning device for conducting the washing process termination determination method based on color change.

{Fig. 10} Fig. 10 is a diagram for describing an alternating current characteristic measurement method.

{Fig. 11} Fig. 11 is a circuit diagram of the alternating current characteristic measurement illustrated in Fig. 10.

{Fig. 12} Fig. 12 is a diagram for describing a chemical cleaning device according to a second embodiment.

{Fig. 13} Fig. 13 is a diagram for describing a chemical cleaning device according to a third embodiment.

{Fig. 14} Fig. 14 is a diagram for describing a chemical cleaning device according to a fourth embodiment.

{Fig. 15} Fig. 15 is a diagram for describing a chemical

cleaning device according to a fifth embodiment.

{Fig. 16} Fig. 16 is a schematic view for describing a chemical cleaning device for conducting washing process termination determination based on pressure change.

{Fig. 17} Fig. 17 is a diagram for describing washing process termination determination based on pressure change.

{Fig. 18} Fig. 18 is a diagram for describing a chemical cleaning device according to an eighth embodiment.

{Fig. 19} Fig. 19 is a diagram for describing a chemical cleaning device according to a ninth embodiment.

{Fig. 20} Fig. 20 is a schematic view of a thermal power generation system.

{Description of Embodiments}

{0059}

A washing liquid used in a chemical cleaning method and a chemical cleaning system of the present invention is an aqueous solution containing a neutral rust removing agent.

The neutral rust removing agent is a chelating agent, a reducing agent, or a mixture of the chelating agent and the reducing agent. Examples of the chelating agent include aminocarboxylic acid-based chelating agents such as aminocarboxylic acids including EDTA, BAPTA, DOTA, EDDS, INN, NTA, DTPA, HEDTA, TTHA, PDTA, DPTA-OH, HIDA, DHEG, GEDTA, CMGA, and EDDS and its salts, oxycarbonic acid-based chelating agents such as oxycarbonic acids including a citric acid, a

gluconic acid, and a hydroxyacetic acid and its salts, and organic phosphorus-based chelating agents such as organic phosphorus acids including ATMP, HEDP, NTMP, PBTC, and EDTMP and its salt. Examples of the reducing agent include various metal ions such as Fe^{2+} , Sn^{2+} , sulfite such as sodium sulfite, organic compounds such as an oxalic acid, a formic acid, an ascorbic acid, and pyrogallol, hydrazine, and hydrogen. The washing liquid containing a neutral rust removing agent has pH of 4 to 8, favorably pH of 5 to 7.

{0060}

A corrosion inhibitor may be added to the neutral rust removing agent. In the washing liquid, the concentration of the chelating agent, the reducing agent, and the corrosion inhibitor is appropriately adjusted so that desired detergency and washing time can be obtained.

{0061}

Further, the washing liquid may contain or may not contain an antifoaming agent for preventing foaming. In the present embodiment, a known antifoaming agent can be used.

{0062}

Hereinafter, embodiments of a chemical cleaning method and a chemical cleaning device of the present invention will be described using a thermal power generation system as an example. Note that the present invention is not limited to the thermal power generation system, and is applicable to

other devices to which hematite adheres.

{0063}

<First Embodiment>

Fig. 1 is a diagram for describing a chemical cleaning device according to a first embodiment. Fig. 1 illustrates a case in which a chemical cleaning device 100 is installed in a thermal power generation system 1 at the time of maintenance. The configuration of the thermal power generation system 1 is similar to that of Fig. 20. In the thermal power generation system 1, hematite that is powder scale adheres to an inside of heat transfer piping such as a water wall tube of a once-through boiler 10, and thermal conductivity of the heat transfer piping is decreased. Therefore, to recover heat transfer performance, the once-through boiler 10 is a device to be washed.

{0064}

The chemical cleaning device 100 of the first embodiment includes a chemical tank 101, a chemical supply line 102 that connects the chemical tank 101 and the once-through boiler 10, a chemical discharge line 103 that connects the chemical tank 101 and the once-through boiler 10, and a control unit 104. The chemical tank 101 accommodates the above-described washing liquid. The control unit 104 is, for example, a computer. The control unit 104 includes a determination unit.

{0065}

Figs. 2(a) and 2(b) illustrate an example of a once-through boiler. Fig. 2(a) is a schematic view of a once-through boiler, and Fig. 2(b) is an enlarged view of the portion surrounded by the circle mark A in Fig. 2(a). A once-through boiler 10a of Fig. 2(a) is configured from a combustion chamber 11a surrounded by a wall surface 12a, and a plurality of water wall tubes. Water wall tubes 13a of the once-through boiler 10a are linear tubes extending in a perpendicular direction to a transverse section of the combustion chamber 11a long the wall surface 12a. The plurality of water wall tubes 13a is arrayed in a horizontal direction along the wall surface 12a. A lower header 14a is installed in a lower portion of the combustion chamber 11a, and lower end portions of the plurality of water wall tubes 13a are connected to the lower header 14a. An upper header is installed in an upper portion of the combustion chamber 11a, and upper end portions of the plurality of water wall tubes 13a are connected to the upper header 15a.

{0066}

Figs. 3(a) and 3(b) are another example of a once-through boiler. Fig. 3(a) is a schematic view of the once-through boiler, and Fig. 3(b) is an enlarged view of the portion surrounded by the circle mark B in Fig. 3(a). A once-through boiler 10b of Figs. 3(a) and 3(b) is different from the once-through boiler 10a of Figs. 2(a) and 2(b) in the shape of a

water wall tube. In the once-through boiler 10b, a plurality of water wall tubes 13b is arranged along a wall surface 12b in a spiral manner under a combustion chamber 11b. The water wall tube 13b branches to a plurality of tubes in a middle position (branching portion 16) of the combustion chamber 11b in the perpendicular direction. The water wall tubes 13b after branching have a linear shape, and extend upward along the wall surface 12b in the perpendicular direction with respect to a transverse section of the combustion chamber 11a.

A lower header 14b is installed in a lower portion of the combustion chamber 11b, and lower end portions of the plurality of water wall tubes 13b are connected to the lower header 14b. An upper header is installed in an upper portion of the combustion chamber 11b, and upper end portions of the plurality of water wall tubes 13b are connected to the upper header 15b.

{0067}

In the chemical cleaning device 100 of the first embodiment, the chemical supply line 102 and the chemical discharge line 103 are connected to the lower header 14a or 14b of the once-through boiler 10 (10a or 10b).

In the chemical supply line 102, a pump 105 and valve V1 are installed. In the chemical discharge line 103, a valve V2 is installed. The pump 105 and the valves V1 and V2 communicate into the control unit 104.

{0068}

Places to which hematite adheres are different depending on water wall tube arranging methods. Hematite has a tendency to be more likely to adhere to a place where a flow velocity of boiler water supply is changed in the water wall tube. For example, in the once-through boiler 10a of Figs. 2(a) and 2(b), a larger amount of hematite adheres to an inner surface of the water wall tube 13a, the inner surface being positioned under the combustion chamber 11a, than other portions. In the once-through boiler 10b of Fig. 3, a larger amount of hematite adheres to an inner surface of the water wall tube 13b of the branching portion 16 than other portions.

{0069}

The chemical cleaning device 100 of the first embodiment further includes a reducing atmosphere adjustment unit. In the chemical cleaning device 100 of the first embodiment, the reducing atmosphere adjustment unit is a reducing atmosphere gas supply unit 110. The reducing atmosphere gas supply unit 110 in Fig. 1 includes a reducing atmosphere gas storage unit 111 and an air supply line 112. The chemical cleaning device 100 includes an exhaust line 113. In the air supply line 112 and the exhaust line 113, valves V3 and V4 are respectively installed. The air supply line 112 and the exhaust line 113 are connected to the upper header 15a or 15b of the once-through boiler 10 (10a or 10b). The valves V3 and V4 are

connected to the control unit 104.

{0070}

The reducing atmosphere gas storage unit 111 is a cylinder that accommodates a reducing atmosphere gas. The reducing atmosphere gas is a gas for adjusting the washing liquid into a reduced state. To be specific, the reducing atmosphere gas is nitrogen, argon, steam, dioxide, a flue gas, or the like. The purity of the reducing atmosphere gas is not necessarily high, and any purity is employable as long as the gas can maintain an oxidation-reduction potential of the washing liquid in a washing process described below to fall within a predetermined range. In a case of using nitrogen as the reducing atmosphere gas, a nitrogen injection facility already installed in the thermal power generation system 1 as the reducing atmosphere gas supply unit 110 can be used, or a nitrogen injection facility may be temporarily or newly installed. The steam or the flue gas as the reducing atmosphere gas can be steam or a flue gas generated in a boiler of adjacent another thermal power generation system.

{0071}

A method of washing and removing hematite adhering to an inside of the once-through boiler, using the chemical cleaning device 100 of the first embodiment, will be described.

The chemical cleaning method of the present embodiment is conducted during a period of a process of building an in-

furnace scaffold and a process of working on devices other than the device to be washed (once-through boiler 10), in periodic inspection of the thermal power generation system, for example.

In conducting the chemical cleaning method of the present embodiment, a valve installed at piping that connects the once-through boiler 10 and the economizer 26 is closed.

{0072}

<Gas Supply Process>

The control unit 104 opens the valves V2 and V3. The reducing atmosphere gas (a nitrogen gas or the like) is fed from the reducing atmosphere gas storage unit 111 to the water wall tubes 13a or 13b of the once-through boiler 10 through the air supply line 112. The air inside the water wall tubes 13a or 13b is discharged to an outside of the system through the chemical discharge line 103. By this process, the air inside the water wall tubes 13a or 13b of the once-through boiler 10 is discharged through the chemical discharge line 103. By the gas supply process, the water wall tubes 13a or 13b are filled with the reducing atmosphere gas.

After a sufficient time to replace the gas has passed, the control unit 104 closes the valves V2 and V3.

{0073}

<Washing Liquid Supply Process>

The control unit 104 starts the pump 105 and opens the

valve V1. The control unit 104 opens the valve V4. The washing liquid in the chemical tank 101 is fed to the once-through boiler 10 through the chemical supply line 102. Accordingly, the inner surfaces of the water wall tubes 13a or 13b are immersed in the washing liquid, and a purge gas inside the water wall tubes 13a or 13b, such as nitrogen of a volume corresponding to the supplied washing liquid, is discharged to an outside of the system through the exhaust line 113.

{0074}

In the present embodiment, the valve of the piping that connects the once-through boiler 10 and the economizer 26 is closed. Therefore, no washing liquid supplied through the chemical supply line 102 to the lower header 14a or 14b can flow into the economizer 26.

{0075}

In the present embodiment, at least regions of the inner surfaces of the water wall tubes 13a or 13b, to which hematite adheres, are immersed in the washing liquid. Especially, regions on the inner surface of the water wall tubes 13a or 13b, to which a large amount of hematite adheres than to other portions, are necessarily immersed in the washing liquid. For example, as illustrated in Fig. 4, the control unit 104 supplies the washing liquid such that a liquid level 18 of the washing liquid is positioned above a region 17 to which a larger amount of hematite adheres than to other portions.

Considering the cost of the chemical cleaning, the washing liquid is filled in the plurality of water wall tubes 13a or 13b up to the upper end portions thereof (connection portions with the upper header 15a or 15b) as an upper limit. In the present embodiment, the washing liquid does not reach the steam-water separator 30 beyond the once-through boiler 10. That is, in the present embodiment, the washing liquid is supplied to only the once-through boiler 10 as the device to be washed.

{0076}

When the place of the region to which hematite adheres, especially, the place of the region 17 to which a larger amount of hematite adheres than to other portions is identified in advance, a necessary amount of the washing liquid in which the hematite adhering region can be immersed can be determined according to the sizes of the water wall tubes 13a or 13b. The control unit 104 stores the necessary amount of the washing liquid, and feeds a predetermined amount of the washing liquid to the once-through boiler 10 according to a steam necessary amount in the washing liquid supply process.

{0077}

<Washing Process>

When the region to which hematite adheres is immersed in the washing liquid, the control unit 104 stops the pump 105,

and closes the valves V1 and V4. In a state where the washing liquid is left to stand, the washing process is conducted where hematite is soaked in the washing liquid.

Although depending on an amount of generation of hematite, a soaking time (washing time) is 24 hours or more, for example. During this washing process, the pressure in the water wall tubes 13a or 13b is not substantially changed and is constant.

{0078}

In the present embodiment, the washing liquid is left to stand during the washing process. Therefore, a washing liquid temperature during the washing process is about equal to an environmental temperature around the water wall tubes 13a or 13b. For example, the environmental temperature around the water wall tubes 13a or 13b is about 20 °C to 40°C. The environmental temperature is close to an outside air temperature, and is not substantially changed during the washing process. Therefore, the washing liquid temperature is also maintained at the temperature about equal to the environmental temperature.

{0079}

Since spaces inside the water wall tubes 13a or 13b are filled with the reducing atmosphere gas due to the gas supply process, the washing liquid during the washing process is maintained in a reduced state. To be specific, the oxidation-

reduction potential of the washing liquid during the washing process can be measured using an oxidation-reduction potentiometer in the middle of the chemical discharge line 103, for example, and the oxidation-reduction potential is maintained from -0.8 V to -0.4 V, both inclusive, on the basis of a silver-silver chloride electrode reference. According to a pH-potential chart, when the oxidation-reduction potential is caused to -0.4 V or less, dissolution efficiency of an iron oxide is enhanced and hematite is dissolved in the washing liquid. Meanwhile, Fe^0 is caused as the oxidation-reduction potential becomes lower. When the oxidation-reduction potential becomes less than -0.8 V, Fe^0 is caused, sludge is deposited, and iron adheres to the water wall tubes 13a or 13b.

{0080}

In a case where the oxidation-reduction potential falls outside a predetermined range, the reducing atmosphere gas is re-filled to maintain the oxidation-reduction potential of the washing liquid. To be specific, the valves V2 and V3 are released. Accordingly, the reducing atmosphere gas is supplied from the reducing atmosphere gas storage unit 111 to the once-through boiler 10, and the washing liquid is fed to the chemical tank 101 through the chemical discharge line 103. Following that, the valves V2 and V3 are closed, the valves V1 and V4 are opened, and the pump 105 is started, so that the

washing liquid in the chemical tank 101 is fed to the once-through boiler 10. Alternatively, the valves V3 and V4 are opened in a state where the valves V1 and V2 are closed, and the reducing atmosphere gas is supplied from the reducing atmosphere gas storage unit 111 to the once-through boiler 10, so that the reducing atmosphere gas is re-filled.

In the case where the oxidation-reduction potential falls outside the predetermined value, the above-described reducing agent may be added to the washing liquid. To be specific, similarly to the above-description, the washing liquid is returned to the chemical tank 101, after the reducing agent is added in the chemical tank 101, the washing liquid is fed to the once-through boiler 10.

Maintenance of the oxidation-reduction potential may be automated on the basis of an instruction from the control unit 104 that monitors the oxidation-reduction potential, or an operator may manually conduct detection and maintenance of the oxidation-reduction potential.

{0081}

Figs. 5 and 6 are results of verification of the effect of the chemical cleaning method of the present embodiment using the water wall tube collected from an actual device. The water wall tube to which hematite adheres is collected from the actual device and is immerse (soaked) in the above-described washing liquid (pH 5 to pH 7) while maintaining the

temperature at 25°C. Conditions of components of the washing liquid are appropriately selected within the range of 3 weight% to 5 weight% of the chelating agent and 1.5 weight% to 2.5 weight% of the reducing agent.

The inner surface of the water wall tube before immersed in the washing liquid is red, and in the SEM photograph (Fig. 5) self-oxidation scale (magnetite (Fe_3O_4)) and hematite were confirmed. Meanwhile, the inner surface of the water wall tube after chemical cleaning is black, and in the SEM photograph (Fig. 6), only the self-oxidation scale was confirmed.

{0082}

A washing effect of the washing liquid was verified using hematite. The washing liquid (pH 5 to pH 7) to which hematite powder is added is put in a container, and the upper portion of the washing liquid is purged with nitrogen and is sealed. The oxidation-reduction potential during the test period falls within the range of -0.8 V to -0.4 V on the basis of a silver-silver chloride electrode reference. The conditions of the components of the washing liquid are selected within the range of 3 weight% to 5 weight% of the chelating agent and 1.5 weight% to 2.5 weight% of the reducing agent. The washing liquid was left to stand for 8 hours while maintaining the temperature at 25°C. As a result, the washing liquid was changed from opaque red brown to nearly a transparent color.

This means that hematite was dissolved in the washing liquid by the soaking.

{0083}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) the iron concentration in the washing liquid, (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube.

{0084}

(1) Determination based on the iron concentration in the washing liquid

In the washing process, the valves V2 and V3 are opened at predetermined periods. The reducing atmosphere gas is fed from the reducing atmosphere gas storage unit 111 to the water wall tubes 13a or 13b of the once-through boiler 10 through the air supply line 112, and the washing liquid in the water wall tubes 13a or 13b is fed from the lower header 14a or 14b to the chemical tank 101 through the chemical discharge line 103. When all of the washing liquid is accommodated in the chemical tank 101, the valves V2 and V3 are closed.

{0085}

<Measurement Process>

A part of the washing liquid collected in the chemical tank 101 is collected. The iron concentration in the washing liquid is measured by quantitative analysis defined in JIS

B8224 using the collected washing liquid. The iron concentration acquired at predetermined periods is input to the determination unit of the control unit 104.

{0086}

<Determination Process>

The numerical value of the iron concentration in the washing liquid is increased over time, and when hematite is completely removed from the water wall tubes 13a or 13b, the concentration becomes saturated to an approximately constant value. The determination unit determines a state in which hematite is eluted and removed, from temporal change of the iron concentration.

{0087}

The iron concentration at which adhering hematite has been substantially eluted can be expected from a basic test or simulation. The iron concentration obtained through a basic test or simulation may be stored in the determination unit as predetermined concentration (determination criterion concentration) that indicates that hematite has been removed. In this case, when the determination unit determines that the iron concentration measured in the measurement process is the determination criterion concentration or more, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process describe below, on the basis of understanding that hematite

has been eluted and removed.

{0088}

Alternatively, removal of hematite may be determined from the amount of change of the iron concentration. When hematite is substantially eluted, change (concentration gradient) of a difference per unit time between a measure value of the iron concentration measured in the measurement process and a previous measured value becomes gradually small. From this fact, the amount of change of the concentration gradient is stored in the determination unit as a determination criterion, and when the determination unit determines that the amount of change of the concentration gradient becomes a value within a predetermined range, the determination unit causes the control unit 104 to terminate the washing process and to conduct a discharge process describe below, on the basis of understanding that hematite has been eluted and removed.

{0089}

For example, the iron concentration C_t in a time T_t is measured in the measurement process, and is input to the determination unit. The determination unit stores the iron concentration C_{t-1} in the previous time (time T_{t-1}) and the iron concentration C_{t-2} in the previous time (time T_{t-2}).

The determination unit acquires concentration gradient ΔC_t per unit time $(= (C_t - C_{t-1}) / (T_t - T_{t-1}))$ of the iron concentration between the time T_t and the time T_{t-1} . The

determination unit stores the concentration gradient ΔC_{t-1} per unit time $(= (C_{t-1} - C_{t-2}) / (T_{t-1} - T_{t-2}))$ of the iron concentration acquired in the previous time.

The determination unit acquires the amount of change Δd_t between the concentration gradient ΔC_t acquired in this time and the concentration gradient ΔC_{t-1} acquired in the previous time. The determination unit determines that the value has reached the determination criterion when the acquired Δd_t falls within the range of the determination criterion stored in advance. For example, the determination criterion is $\pm 20\%$. In a case where deposition of hematite in the device 10 to be washed is relatively uniform, the determination criterion is set to $\pm 10\%$, so that determination accuracy can be improved.

{0090}

When the iron concentration most newly input to the measurement unit is determined to be less than the determination criterion, or when the amount of change of the concentration gradient is determined to be larger than the predetermined range, the determination unit causes the control unit 104 to continue the washing process. The control unit 104 feeds the washing liquid in the chemical tank 101 to the once-through boiler 10 in a process similar to the washing liquid supply process.

{0091}

In the present embodiment, in the measurement process,

the oxidation-reduction potential of the washing liquid is measured at the same time with the measurement of the iron concentration, and the oxidation-reduction potential of the washing liquid falls outside the predetermined range, adjustment of the components of the washing liquid may be adjusted by putting the reducing agent to the washing liquid in the chemical tank 101.

{0092}

(2) Determination based on color change

In the present determination method, determination is made by observing the color change of any of (A) a test piece to which hematite adheres, or (B) the water wall tube.

{0093}

(2-A) Determination using a test piece

The test piece to which hematite adheres is prepared.

The test piece is the water wall tube cut into two pieces along an axial direction, as illustrated in Fig. 7, and hematite adheres to an inner wall surface. Hematite, the amount of which is about equal to the amount of hematite adhering to the once-through boiler 10 (device to be washed) being washed, adheres to this test piece (cut test piece 120). For example, the test piece is prepared by cutting the water wall tube collected from the same position at the time of previous maintenance, or the water wall tube collected from another plant operated in a similar condition.

The test piece may be a plate member (plate test piece) having the same material quality as the water wall tube, and having one surface to which hematite adheres, the amount of hematite being equal to the amount of hematite adhering to the water wall tube.

Further, the test piece may be the water wall tube collected as described above (which is a tubular test piece but is not cut along the axial direction like the above cut test piece).

{0094}

In the present determination, the surface of the test piece to which hematite adheres is immersed in the washing liquid in the washing process.

As an immersing method, a plurality of the cut test pieces or the plate test pieces is immersed in the washing liquid stored in the chemical tank 101 at the same time of the start of washing.

In this case, the reducing atmosphere gas is made able to be fed into the chemical tank 101, and the washing liquid inside the chemical tank 101 is desirably adjusted to have an oxidation-reduction potential similar to the water wall tubes 13a or 13b while the test pieces are immersed.

{0095}

As another immersing method, a transparent plate (for example, acrylic plate) 121 is arranged on a cut surface of

the cut test piece 120, as illustrated in Fig. 8, and a washing liquid containing the rust removing agent having the same concentration as the washing liquid fed to the once-through boiler 10 is injected into a space 122 formed in one end surface of the cut test piece 120 by arrangement of a plate member (not illustrated in Fig. 8), so that the surface to which hematite adheres is immersed in the washing liquid. Pouring of the washing liquid is favorably performed approximately at the same time as the start of the washing process.

In this case, the washing liquid injected into the cut test piece 120 is favorably adjusted to have an oxidation-reduction potential similar to the water wall tubes 13a or 13b with the reducing atmosphere gas.

{0096}

As another immersing method, a by-pass portion 130 is installed on an upstream side of the valve V1 of the chemical supply line 102, as illustrated in Fig. 9, and a tubular test piece 132 is connected to a middle position of a by-pass pipe 131 of the by-pass portion 130. In the washing liquid supply process, when the pump 105 is started and the valve V1 is opened, a part of the washing liquid passing through the chemical supply line 102 flows into the by-pass portion 130, and an inner wall surface of the tubular test piece 132 is immersed in the washing liquid.

In this case, the reducing atmosphere gas is also supplied to reach the by-pass portion 130 in the gas supply process, and the washing liquid in the tubular test piece 132 while being immersed is favorably adjusted to have an oxidation-reduction potential similar to the water wall tubes 13a or 13b.

{0097}

<Observation Process>

In the washing process, one of the test pieces immersed in the washing liquid in the chemical tank 101 is taken out of the washing liquid at predetermined time intervals. The color of the surface of the taken out test piece, to which hematite adheres, is observed. The observation is visually performed by an operator or is performed using a CCD camera. In the case of visual observation, the operator inputs a determination result of color change to the determination unit. In the case of observation with a CCD camera, measured data is transmitted to the determination unit.

{0098}

In a case where the surface to which hematite adheres is immersed in the washing liquid, as illustrated in Fig. 8, the visual observation or the observation with a CCD camera is conducted from the transparent plate 121 side at predetermined periods.

{0099}

In the case where the by-pass portion 130 is installed, as illustrated in Fig. 9, the inner wall surface of the tubular test piece 132 is observed using a CCD camera at predetermined periods. To be specific, an observation hole is drilled in the tubular test piece 132, a view port that enables reflection light from an observation portion to enter the CCD camera is inserted into the observation hole, and the inner wall surface immersed in the washing liquid is observed. The measured data is transmitted to the determination unit.

{0100}

<Determination Process>

Hematite is roughly red. When removal of hematite progresses, a natural oxidation layer (magnetite: roughly black) as a ground layer or a ground metal layer (roughly silver) is exposed, and thus a color tone is changed.

The determination unit determines that hematite has been removed when a color derived from hematite is not observed. The determination unit causes the control unit 104 to terminate the washing process, and to conduct the discharge process described below. The determination unit causes the control unit 104 to continue the washing process when the color derived from hematite is observed.

{0101}

The determination unit separates RGB components of a measured data signal, and extracts only the R component, or

the R component and the B component. The determination unit determines a state where hematite is eluted or removed, from temporal change of the R component, or temporal change of a ratio of the R component and the B component (R component/B component).

{0102}

To be specific, the determination unit stores a determination criterion of a ratio of an R component value to an initial value (R component measured value/R component initial value), or a ratio of a value of the R component/B component to an initial value ((R component/B component measured value)/(R component/B component initial value)). To be specific, this determination criterion is a value within a range of 1/5 to 1/10. Since the measured value of the R component of the R component/B component differs according to a deposition state of hematite, it is desirable to determine the determination criterion in a basic test.

When the ratio of the R component value to the initial value or the ratio of the value of the R component/B component to the initial value is the determination criterion or less, the determination unit determines that the color derived from hematite is not observed. When the color derived from hematite is not observed, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of

understanding that hematite has been eluted and removed.

{0103}

When the ratio of the R component value to the initial value or the ratio of the value of the R component/B component to the initial value is larger than the determination criterion, hematite remains. Therefore, determination unit causes the control unit 104 to continue the washing process.

{0104}

(2-B) Determination using a water wall tube

In the washing process, the valves V2 and V3 are opened at predetermined periods. The reducing atmosphere gas is fed from the reducing atmosphere gas storage unit 111 to the water wall tubes 13a or 13b of the once-through boiler 10 through the air supply line 112, and the washing liquid in the water wall tubes 13a or 13b is fed from the lower header 14a or 14b to the chemical tank 101 through the chemical discharge line 103. When all of the washing liquid is accommodated in the chemical tank 101, the valves V2 and V3 are closed.

{0105}

<Observation Process>

In a vicinity of the region 17 of the water wall tubes 13a or 13b, to which hematite adheres, an observation hole is drilled. The observation hole is formed in a surface of the water wall tubes 13a or 13b at an opposite side to the combustion chamber 11a or 11b. A view port for CCD camera is

inserted into the observation hole, and the inner wall surface is observed.

{0106}

<Determination Process>

The determination unit determines a removal state of hematite from the color derived from hematite in a process similar to the description in (2-A), and causes the control unit 104 to continue or terminate the washing process.

{0107}

Note that the observation hole formed in a surface of the water wall tubes 13a or 13b to make determination using a CCD camera is recovered by being filled out by welding or the like after the chemical cleaning is terminated.

{0108}

(3) Determination based on an analysis result of an internal state from an outside of the water wall tube

In the present method, a state of an inside of the water wall tube is analyzed by pipe wall thickness measurement with ultrasonic waves or alternating current characteristic measurement.

{0109}

(3-A) Ultrasonic measurement

Before the chemical cleaning, an ultrasonic probe is attached to an outside of the region of the water wall tube, to which hematite adheres. The region to which hematite

adheres is identified by collecting the water wall tube and observing the inner wall surface at the time of previous maintenance. Alternatively, the region is identified by bringing the probe to scan along a water circulating direction from an outside of the water wall tube and measuring the pipe wall thickness of the water wall tube to which hematite adheres before the chemical cleaning.

{0110}

<Measurement Process>

The ultrasonic measurement of the water wall tube is conducted at predetermined time intervals during the washing process. Measured value (the thickness of the water wall tube) acquired in the measurement process is transmitted to the determination unit.

{0111}

<Determination Process>

The measured value is decreased when hematite is eluted and removal progresses, and the measured value by ultrasonic waves becomes constant as the pipe wall thickness of the water wall tube with no adhering hematite when hematite is completely removed. The determination unit determines the removal state of hematite, from temporal change of the measured value by ultrasonic waves.

{0112}

The pipe wall thickness of the water wall tube that indicates that adhering hematite is substantially eluted can be expected from a basic test or simulation. The pipe wall thickness obtained through a basic test or simulation is stored in the determination unit as a determination criterion indicating that hematite has been removed. In this case, when the determination unit determines that the pipe wall thickness measured in the measurement process becomes the determination criterion or less, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of understanding that hematite has eluted and removed.

{0113}

Alternatively, removal of hematite may be determined from the amount of change of the measured value of the pipe wall thickness. When hematite is substantially eluted, a difference between a pipe wall thickness value obtained in the measurement process and a pipe wall thickness obtained in the previous measurement process becomes gradually small. From this fact, the amount of change of pipe wall thickness change gradient that is an inclination of change of pipe wall thickness per unit time is stored in the determination unit as a determination criterion. When the determination unit determines that the amount of change of the pipe wall thickness change gradient becomes a value within the

predetermined range, the determination unit cause the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of understanding that hematite is eluted or removed.

{0114}

Specific determination is performed according to the same idea as the method described in (1) determination based on the iron concentration in the washing liquid. In the case of ultrasonic measurement, the determination criterion is $\pm 20\%$. Further, in a case where deposition of hematite is relatively uniform in the device 10 to be washed, the determination criterion is set to $\pm 10\%$, so that determination accuracy can be improved.

{0115}

When the determination unit determines that the pipe wall thickness value measured in the measurement process has not reached the determination criterion, or when the determination unit determines that the amount of change of the pipe wall thickness change gradient is larger than the predetermined range, the determination unit causes the control unit 104 to continue the washing process.

{0116}

(3-B) Alternating current characteristic measurement

A current characteristic evaluation device 140 is installed outside the region of the water wall tube, to which

hematite adheres, before the chemical cleaning, as illustrated in Fig. 10. Two terminals 141 are installed to be separated in the axial direction of the water wall tube 13 (13a or 13b), and an LCR meter 142 is installed between the terminals 141. The distance between the terminals 141 is set to about 1 m to 5 m so that the alternating current characteristic can be easily distinguished from a direct current characteristic of the water wall tube 13 (13a or 13b). A network analyzer may be installed in place of the LCR meter 142.

{0117}

<Measurement Process>

The alternating current characteristic measurement of the water wall tube is conducted at predetermined time intervals during the washing process.

Fig. 11 is a circuit diagram of a case where the current characteristic evaluation device 140 is installed, as illustrated in Fig. 10. The water wall tube 13 and the washing liquid inside the water wall tube are expressed by resistors R1 and R3, respectively. The region 17 to which hematite adheres is expressed by resistors R2a and R2b, and capacitor capacitance C1 and C2.

{0118}

Hematite (oxide) is a resistance component. When removal of hematite progresses, the capacitor capacitance (C1 and C2) of hematite is decreased, and thus reactance of the circuit is

decreased. The LCR meter 141 measures the reactance of the water wall tube 13 at predetermined time intervals. The value of the reactance acquired in the measurement process is transmitted to the determination unit.

{0119}

<Determination Process>

When the removal of hematite progresses, the measured value of the reactance is decreased. When hematite is completely removed, the measured reactance becomes constant. The determination unit determines the removal state in which hematite is eluted, from the temporal change of the reactance.

{0120}

The reactance of the water wall tube indicating that adhering hematite is substantially eluted can be expected from a basic test or simulation. The reactance obtained through a basic test or simulation is stored in the determination unit as a determination criterion indicating that hematite has been removed. In this case, when the determination unit determines that the reactance measured in the measurement process becomes the determination criterion or less, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of understanding that hematite has been eluted and removed.

{0121}

Alternatively, removal of hematite may be determined from the amount of change of the measured value of the reactance. In a case where hematite is substantially eluted, a difference between the reactance obtained in the measurement process and the reactance obtained in the previous measurement process becomes gradually small. The amount of change of reactance change gradient per unit time is stored in the determination unit as a determination criterion. When the determination unit determines that the amount of change of the reactance change gradient becomes a value within a predetermined range, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of understanding that hematite has been eluted and removed.

{0122}

Specific determination is performed according to the same idea as the method described in (1) determination based on the iron concentration in the washing liquid. In the case of measuring the alternating current characteristic, the determination criterion is $\pm 20\%$. Further, in a case where deposition of hematite is relatively uniform in the device 10 to be washed, the determination criterion is set to $\pm 10\%$, so that determination accuracy can be improved.

{0123}

When the determination unit determines that the reactance

measured in the measurement process has not reached the determination criterion, or when the determination unit determines that the amount of change of the reactance change gradient is larger than the predetermined range, the determination unit causes the control unit 104 to continue the washing process.

{0124}

<Discharge Process>

The control unit 104 opens the valve V2. The washing liquid in the water wall tubes 13a or 13b is fed from the lower header 14a or 14b to the chemical tank 101 through the chemical discharge line 103 and is collected. Accordingly, the chemical cleaning method of the present embodiment is terminated.

If the rust removing agent remains in the collected washing liquid, the washing component (the concentration of the rust removing agent) may be re-adjusted and re-used in the next chemical cleaning.

{0125}

According to the above-described method, the washing liquid containing a neutral rust removing agent is used. Therefore, even if the washing process is conducted in a soaked state, the inner surface of the water wall tube 13a or 13b immersed in the washing liquid do not corrode, and hematite can be dissolved in the washing liquid.

As described in Figs. 5 and 6, the present embodiment is not the method of separating and removing hematite by eluting the magnetite layer that is natural oxide scale. Therefore, occurrence of sludge is suppressed. Especially, in the thermal power generation system 1, the piping of the water wall tubes of the once-through boiler 10 is long and the shape is complicated. Therefore, when the sludge occurs, the sludge may be integrated in the middle of the piping and block the piping. If hematite is dissolved in the washing liquid and removed from the water wall tubes 13a or 13b, like the present embodiment, the eluted hematite can be discharged together with discharge of the washing liquid after the chemical cleaning. Therefore, for example, in the thermal power generation system 1 that employs the present embodiment, a facility to remove the sludge such as a filter is not necessary and another process such as washing to remove the sludge is also not necessary.

{0126}

<Second Embodiment>

Fig. 12 is a diagram for describing a chemical cleaning device according to a second embodiment.

In a chemical cleaning device 200 of the second embodiment, a chemical supply line 202 and a chemical discharge line 203 are connected to a lower header 14a or 14b of a once-through boiler 10, similarly to the first

embodiment. The chemical supply line 202 and the chemical discharge line 203 are connected to a chemical tank 201. An exhaust line 213 is connected to an upper header 15a or 15b of the once-through boiler.

{0127}

The chemical cleaning device 200 includes a reducing atmosphere gas supply unit 210 on a downstream side of a pump 205 of the chemical supply line 202 as a reducing atmosphere adjustment unit. The reducing atmosphere gas supply unit 210 is connected to a control unit 204.

{0128}

The reducing atmosphere gas supply unit 210 of the second embodiment is a micro bubble generator. The micro bubble generator is a device that injects bubbles into a liquid. In the present embodiment, a gas to be injected into the liquid (washing liquid) as the bubbles is a reducing atmosphere gas exemplified in the first embodiment.

{0129}

Although not illustrated in Fig. 12, a reducing atmosphere gas storage unit and an air supply line connected to the once-through boiler 10 may be installed, similarly to Fig. 1.

{0130}

A chemical cleaning method using the chemical cleaning device 200 of the second embodiment will be described. In the

present embodiment, in conducting the chemical cleaning method, a valve installed at the piping that connects the once-through boiler 10 and an economizer 26 is closed.

{0131}

<Washing Liquid Supply Process/Gas Supply Process>

The control unit 204 closes a valve V2. The control unit 204 starts the pump 205 and the reducing atmosphere gas supply unit 210, and opens a valve V1. The washing liquid in the chemical tank 201 is conveyed to the reducing atmosphere gas supply unit 210 through the chemical supply line 202. The reducing atmosphere gas supply unit 210 injects bubbles of the reducing atmosphere gas into the washing liquid. The washing liquid containing the bubbles is supplied to the water wall tubes 13a or 13b of the once-through boiler 10 through the chemical supply line 202.

{0132}

The bubbles in the washing liquid are released from the washing liquid in the water wall tubes 13a or 13b, and are stored in an upper space of the washing liquid supplied to the water wall tubes 13a or 13b. The control unit 204 opens a valve V4, and the air in the water wall tubes 13a or 13b is released to an outside of the system through the exhaust line 213. In this way, a purge gas atmosphere inside the water wall tubes 13a or 13b is replaced with the reducing atmosphere gas.

{0133}

As described above, in the second embodiment, an independent gas supply process is unnecessary, unlike the first embodiment, and the replacement of the gas in the water wall tubes 13a or 13b is performed together with the washing liquid supply process.

{0134}

<Washing Process>

When at least a region to which hematite adheres (especially, a region 17 to which a larger amount of hematite adheres than to other portions) is immersed in the washing liquid, the control unit 204 stops the pump 205 and the reducing atmosphere gas supply unit 210, and closes the valves V1 and V4. In a state where the washing liquid is left to stand, soaking washing treatment of hematite is conducted. In the present embodiment, the washing liquid in the water wall tubes 13a or 13b has a temperature about equal to an environmental temperature around the water wall tubes 13a or 13b, and an oxidation-reduction potential is maintained from -0.8 V to -0.4 V, both inclusive, on the basis of a silver-silver chloride electrode reference.

{0135}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) iron concentration in the washing liquid, (2) color change of a

hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, similarly to the first embodiment. When the determination unit determines that hematite has been eluted and removed in a determination process, the determination unit causes the control unit 104 to terminate the washing process and to conduct a discharge process.

{0136}

<Discharge Process>

The washing liquid in the water wall tubes 13a or 13b is collected in the chemical tank 201 in a process similar to the first embodiment. Accordingly, the chemical cleaning method of the present embodiment is terminated.

{0137}

In a case of using a washing liquid not containing an antifoaming agent in the chemical cleaning method of the first and second embodiments, the washing liquid foams as the washing liquid is fed to the water wall tubes 13a or 13b, and foaming washing liquid adheres to a region where hematite is generated. A period of time for which hematite is in contact with foaming washing liquid becomes long, so that detergency is improved. Further, with the foaming washing liquid, an amount of use of the washing liquid is decreased.

{0138}

<Third Embodiment>

Fig. 13 is a diagram for describing a chemical cleaning device according to a third embodiment.

In a chemical cleaning device 300 of the third embodiment, a chemical supply line 302 and a chemical discharge line 303 are connected to a lower header 14a or 14b of a once-through boiler 10, similarly to the first embodiment. The chemical supply line 302 and the chemical discharge line 303 are connected to a chemical tank 301.

{0139}

The chemical cleaning device 300 includes a reducing atmosphere regulator supply unit 310 as a reducing atmosphere adjustment unit. The reducing atmosphere regulator supply unit 310 includes a reducing atmosphere regulator storage unit 311 and a reducing atmosphere regulator supply line 312. The reducing atmosphere regulator storage unit 311 accommodates a reducing atmosphere regulator. The reducing atmosphere regulator is hydrazine, an L-ascorbic acid, or a Sulphur-based reducing agent, for example.

The reducing atmosphere regulator supply unit 310 is connected to the chemical supply line 302 on a downstream side of a pump 305. A valve V5 is installed at the reducing atmosphere regulator supply line 312. The valve V5 is connected to a control unit 304.

{0140}

Although not illustrated in Fig. 13, a reducing

atmosphere gas storage unit, an air supply line, and an exhaust line to be connected to the once-through boiler 10 may be installed, similarly to Fig. 1.

{0141}

A method of washing and removing hematite adhering to an inside of the once-through boiler, using the chemical cleaning device 300 of the third embodiment, will be described. In conducting the chemical cleaning method of the present embodiment, a valve installed at piping that connects the once-through boiler 10 and the economizer 26 is closed.

{0142}

<Washing Liquid Supply Process>

The control unit 304 closes a valve V2. The control unit 304 starts the pump 305, and opens valves V1 and V5. A reducing atmosphere regulator is input from the reducing atmosphere regulator supply unit 310 into a washing liquid while the washing liquid in the chemical tank 301 passes through the chemical supply line 302. The washing liquid into which the reducing atmosphere regulator is input is fed to water wall tubes 13a or 13b of the once-through boiler 10.

{0143}

<Washing Process>

When at least a region to which hematite adheres is immersed in the washing liquid, the control unit 304 stops the pump 305 and closes the valves V1 and V5. In a state where

the washing liquid is left to stand, soaking washing treatment of hematite is conducted.

{0144}

In the present embodiment, the washing liquid in the water wall tubes 13a or 13b has a temperature about equal to an environmental temperature around the water wall tubes 13a or 13b. The reducing atmosphere regulator is input from the reducing atmosphere regulator supply unit 310 into the washing liquid, so that an oxidation-reduction potential of the washing liquid is maintained from -0.8 V to -0.4 V, both inclusive, on the basis of a silver-silver chloride electrode reference. The control unit 304 adjusts the degree of opening of the valve V5 to obtain the amount of input of the reducing atmosphere regulator by which a steam oxidation-reduction potential can be obtained.

{0145}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) iron concentration in the washing liquid, (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, similarly to the first embodiment. When the determination unit determines that hematite has been eluted and removed in a determination process, the determination unit causes the control unit 104 to terminate the washing process and to

conduct a discharge process.

{0146}

<Discharge Process>

The washing liquid in the water wall tubes 13a or 13b is collected to the chemical tank 301 through the chemical discharge line 303 in a process similar to the first embodiment. Accordingly, the chemical cleaning method of the present embodiment is terminated.

{0147}

In a case where a large amount of hematite adheres, variation of the oxidation-reduction potential due to dissolving of hematite becomes large. By additionally inputting the reducing atmosphere regulator into the washing liquid like the present embodiment, the oxidation-reduction potential can be easily adjusted to fall within the range of -0.8 V to -0.4 V.

{0148}

<Fourth Embodiment>

Fig. 14 is a diagram for describing a chemical cleaning device according to a fourth embodiment.

A chemical cleaning device 400 according to the fourth embodiment includes, similarly to the chemical cleaning device of the first embodiment, a chemical tank 401, a chemical supply line 402, a chemical discharge line 403, a control unit 404, a pump 405, a reducing atmosphere gas storage unit 411

and an air supply line 412 as a reducing atmosphere gas supply unit 410, and an exhaust line 413.

In the chemical cleaning device 400, a circulation loop 406 is installed over the pump 405 of the chemical supply line 402.

Note that the circulation loop can be provided in the chemical cleaning devices of the second and third embodiments.
{0149}

In a washing liquid supply process, the temperature of a washing liquid rises as passing through the pump 405. A part of the washing liquid having passed through the pump 405 flows into the circulation loop 406, and is conveyed to a chemical common line on an upstream side of the pump 405. In doing so, the washing liquid with a raised temperature is conveyed to water wall tubes 13a or 13b of a once-through boiler 10, and the washing process is conducted at a higher temperature than the first to third embodiments (to be specific, higher than the environmental temperature around the water wall tubes 13a or 13b, and about the environmental temperature + 10°C, or less).

{0150}

As the temperature in the washing process is made higher, a reaction between the washing liquid and hematite, and dissolving into the washing liquid are facilitated. According to the present embodiment, temperature rise of the washing

liquid can be realized with a simple configuration, without installing a temperature raiding facility. Further, a temperature difference between the environmental temperature and the washing liquid temperature is small. Therefore, with the configuration of the present embodiment, the temperature of the washing liquid can be maintained higher than the environmental temperature for a long time. As a result, detergency can be further enhanced.

{0151}

In the present embodiment, termination of the washing process is determined by a method similar to the first embodiment.

{0152}

<Fifth Embodiment>

Fig. 15 is a diagram for describing a chemical cleaning device according to a fifth embodiment.

A chemical cleaning device 500 according to the fifth embodiment includes, similarly to the chemical cleaning device of the first embodiment, a chemical tank 501, a chemical supply line 502, a chemical discharge line 503, a control unit 504, a pump 505, a reducing atmosphere gas storage unit 511 and an air supply line 512 as a reducing atmosphere gas supply unit 510, and an exhaust line 513.

The chemical cleaning device 500 further includes a water supply unit 520. The water supply unit 520 includes a water

tank 521 and a water supply line 522. The water tank 521 accommodates water therein. A water filling pump 523 and a valve V6 are installed in the water supply line 522. The water supply line 522 is connected to a lower header 14a or 14b.

{0153}

A method of washing and removing hematite adhering to an inside of a once-through boiler, using the chemical cleaning device 500 of the fifth embodiment, will be described. In conducting the chemical cleaning method of the present embodiment, a valve installed at piping that connects the once-through boiler 10 and the economizer 26 is closed.

{0154}

<Gas Supply Process>

In a process similar to the first embodiment, a reducing atmosphere gas is supplied from the reducing atmosphere gas storage unit 511 to water wall tubes 13a or 13b through the air supply line 512, and the water wall tubes 13a or 13b are filled with the reducing atmosphere gas.

{0155}

<Washing Liquid Supply Process>

The control unit 504 starts the pump 505, and opens valves V1 and V4. A washing liquid in the chemical tank 501 is fed to a once-through boiler 10 through the chemical supply line 502.

{0156}

After a predetermined amount of washing liquid has fed, the control unit 504 stops the pump 505 and closes the valve V1. Next, the control unit 504 starts the water filling pump 523, and opens the valve V6. Accordingly, the water in the water tank 521 is fed to the water wall tubes 13a or 13b of the once-through boiler 10 through the water supply line 522.

{0157}

By adjusting flow velocities of the washing liquid and the water, a layer of the washing liquid comes to an upper side in a vertical direction and a layer of the water comes to a lower side in the vertical direction, and a water level in the water wall tubes 13a or 13b rises in a state where the washing liquid layer and the water layer are at least partially separated. In the present embodiment, the control unit 504 feeds predetermined amounts of the washing liquid and the water from the chemical tank 501 and the water tank 521 to the water wall tubes 13a or 13b such that a region 17 to which a larger amount of hematite adheres than to other portions in the water wall tubes 13a or 13b is immersed in the washing liquid layer.

{0158}

<Washing Process>

When the region 17 to which a larger amount of hematite adheres than to other portions is immersed in the washing

liquid, the control unit 504 stops the water filling pump 523, and closes the valves V4 and V6. Soaking and washing of hematite are conducted in a state where the washing liquid is left to stand. In the present embodiment, the temperature of the washing liquid during the washing process is about equal to an environmental temperature around the water wall tubes 13a or 13b, and an oxidation-reduction potential of the washing liquid during the washing process is maintained from -0.8 V to -0.4 V, both inclusive (on the basis of a silver-silver chloride electrode reference).

{0159}

In the present embodiment, the state in which the washing liquid layer and the water layer are separated needs to be secured during the washing process. Therefore, termination of the washing process is determined on the basis of any of (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, described in the first embodiment. When a determination unit determines that hematite has been eluted and removed in the determination process, the determination unit causes the control unit 104 to terminate the washing process and to conduct a discharge process.

{0160}

<Discharge Process>

The washing liquid in the water wall tubes 13a or 13b is

fed to the chemical tank 501 in a process similar to the first embodiment. Accordingly, the chemical cleaning method of the present embodiment is terminated.

In the washing liquid collected in the chemical tank 501, rust removing agent concentration is decreased. Therefore, a new washing liquid is added and the washing liquid is re-used, or the washing liquid is discharged and disposed from the chemical tank 501.

{0161}

According to the method of the present embodiment, the region 17 to which a larger amount of hematite adheres than to other portions is immersed in the washing liquid and is intensively removed. Therefore, the amount of use of the washing liquid can be significantly reduced and thus washing cost can be reduced.

{0162}

<Sixth Embodiment>

A chemical cleaning device of the sixth embodiment has the same configuration as the first embodiment except that a washing liquid is accommodated in microcapsules.

The microcapsule is obtained such that the washing liquid is packaged in a water-soluble capsule. The material quality of the microcapsule is, for example, a water-soluble polymer such as dextrin, processed starch, gelatin, gum arabic, sodium alginate, or carrageenan. The size of the microcapsule is,

for example, about 0.5 mm to 2 mm in diameter. The microcapsule is manufactured by a spray-drying method, a spray-cooling method, or the like, for example.

{0163}

In the chemical cleaning device of the sixth embodiment, a microcapsule supply unit is installed on an upstream side of a pump 105 of a chemical supply line 102. The microcapsule supply unit includes a tank that accommodates the microcapsules. The microcapsules are accommodated in the tank in a state of being dispersed in a conveying liquid (for example, water).

{0164}

In the sixth embodiment, a gas supply process, a washing liquid supply process, a washing process, and a discharge process are conducted, similarly to the first embodiment. In the washing liquid supply process of the sixth embodiment, the conveying liquid containing the microcapsules is supplied into the washing liquid circulated in the chemical supply line 102 upon start of a pump installed in a passage that connects the microcapsule supply unit and the chemical supply line 102, and the washing liquid containing the microcapsules is supplied to the water wall tubes 13a or 13b. The microcapsules are moved upward in the water wall tubes 13a or 13b, and are deposited near a liquid level. When the capsules of the microcapsules are dissolved in the conveying liquid, the washing liquid is

released, and a layer of the foamed washing liquid is formed near the liquid level. Especially, dispersion concentration of the microcapsules (the amount of the washing liquid) and the liquid level height (the amount of the conveying liquid supplied by the control unit 104) are appropriately adjusted such that a region 17 to which a larger amount of hematite adheres than to other portions is immersed in the washing liquid.

{0165}

According to the method of the present embodiment, the region in which a larger amount of hematite is generated than other portions can be easily immersed in the washing liquid. Therefore, the amount of use of the washing liquid can be significantly reduced, and thus washing cost can be further reduced.

{0166}

Note that the sixth embodiment is applicable to the chemical cleaning methods and the chemical cleaning devices of the second to fifth embodiment.

{0167}

<Seventh Embodiment>

A chemical cleaning method according to a seventh embodiment will be described using a chemical cleaning device 100 of Fig. 1. In the chemical cleaning method of the seventh embodiment, a gas supply process, a washing liquid supply

process, and a discharge process are conducted, similarly to the first embodiment, except for a washing process.

{0168}

In the washing process in the chemical cleaning method of the seventh embodiment, when a region to which hematite adheres is immersed in a washing liquid, a control unit 104 stops a pump 105, and closes valves V1 and V4.

{0169}

The control unit 104 opens a valve V2. With the open of the valve V2, the washing liquid is fed to return to a chemical tank 101 through a chemical discharge line 103. Therefore, a liquid level of the washing liquid in water wall tubes 13a or 13b is decreased. Next, the control unit 104 closes the valve V2, opens the valve V1, and starts a pump 105. Accordingly, the washing liquid in the chemical tank 101 is fed to the water wall tubes 13a or 13b of a once-through boiler 10 through a chemical supply line 102, and the liquid level of the washing liquid in the water wall tubes 13a or 13b rises. The control unit 104 conducts discharge and feed of the washing liquid at predetermine periods.

{0170}

The amount of discharge of the washing liquid here may be a part or all of the washing liquid. When the mount of discharge of the washing liquid is changed, the amount of change of the liquid level can be changed. The amount of

discharge of the washing liquid, that is, the amount of change of the liquid level is favorably appropriately set in consideration of the size of the region to which a larger amount of hematite adheres than to other portions, and washing efficiency. The control unit 104 discharges and feeds a predetermined amount of the washing liquid corresponding to the amount of change of the liquid level.

Further, a period of the discharge and feed of the washing liquid and a period of leaving the washing liquid may be periodically and alternately conducted.

{0171}

When the discharge and feed of the washing liquid is repeated, stirring of the washing liquid near the liquid level in the water wall tubes 13a or 13b occurs, and a flow velocity is given to the washing liquid. As a result, detergency is improved, and washing efficiency of hematite is increased.

{0172}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) iron concentration in the washing liquid, (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, similarly to the first embodiment. When a determination process determines that hematite has been removed, a determination unit causes the control unit 104 to terminate

the washing process and to conduct a discharge process.

{0173}

Further, in the present embodiment, determination of termination of the washing process may be made on the basis of (4) pressure change.

(4) Determination based on pressure change

In the determination based on a pressure change signal, a pressure gauge 150 is installed in a middle position of the chemical discharge line 103, as illustrated in Fig. 16.

{0174}

At the time of a feeding process in the washing process, the number of rotation of the pump 105 or the degree of opening of the valve V1 is increased/decreased at a predetermined frequency. In doing so, the amount of feed of the washing liquid is increased/decreased at a predetermined frequency. Therefore, the liquid level of the washing liquid in the water wall tubes 13a or 13b vibrates.

{0175}

<Measurement Process>

In the discharge process in the washing process, the pressure gauge 150 measures a pressure of the washing liquid that passes through the chemical discharge line 103. A pressure value is transmitted to the determination unit.

{0176}

<Determination Process>

When the liquid level of the washing liquid vibrates in the feeding process, the pressure measured with the pressure gauge 150 in the discharge process reflects the vibration state of the liquid level and is periodically changed. This change of the pressure varies according to an adhering state of hematite. That is, when removal of hematite progresses by washing, a friction coefficient between the washing liquid and hematite is changed. Therefore, the pressure change varies over time. When hematite is removed from the water wall tube, a frequency of feed of the washing liquid in the feeding process and a frequency of the pressure change in the discharge process coincide with each other. Therefore, a difference between a phase of periodical feed of the washing liquid in the feeding process and a phase of the pressure change in the discharge process becomes constant.

{0177}

The determination process is conducted in one of two steps below.

(Step 4-A)

The determination unit acquires a waveform of the amount of feed in the feeding process and a waveform of change of the pressure value acquired in the measurement process, as exemplarily illustrated in Fig. 17. The determination unit compares the waveform of the amount of feed and the waveform of the pressure change and determines a removal state where

hematite is eluted.

{0178}

To be specific, the difference between the phase of the waveform of the amount of feed in a case where adhering hematite is substantially eluted and the phase of the waveform of the pressure change (a phase difference, illustrated in Fig. 17) can be expected from a basic test or simulation expect. The phase difference obtained through a basic test or simulation is stored in the determination unit as a determination criterion indicating that hematite has been removed. In this case, when the determination unit determines that the phase difference measured in the measurement process becomes the determination criterion or less, the determination unit causes the control unit 104 to terminate the washing process and to conduct a discharge process, on the basis of understanding that hematite has been eluted and removed.

{0179}

Alternatively, removal of hematite may be determined from the amount of change of the phase difference. In a case where hematite is substantially eluted, a difference between the obtained phase difference and the previously obtained phase difference becomes gradually small. The amount of change of the phase difference change gradient that is an inclination of change of the phase difference per unit time is stored in the determination unit as a determination criterion. When the

determination unit determines that the amount of change of the phase difference change gradient becomes a value within the predetermined range, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below.

{0180}

Specific determination is performed according to the same idea as the method described in (1) determination based on the iron concentration in the washing liquid. When determination is made using the phase difference, the determination criterion is $\pm 20\%$. Further, in a case where deposition of hematite is relatively uniform in the device 10 to be washed, the determination criterion is set to $\pm 10\%$, so that determination accuracy can be improved.

{0181}

When the determination unit determines that the phase difference is larger than the determination criterion, or when the determination unit determines that the amount of change of the phase difference change gradient is larger than the predetermined range, the determination unit causes the control unit 104 to continue the washing process.

{0182}

(Step 4-B)

The determination unit acquires the waveform of the change of the pressure value acquired in the measurement

process, and determines the removal state of hematite from change with time of a period and amplitude of the waveforms.

{0183}

To be specific, the period and the amplitude of the waveform of the pressure value when adhering hematite is substantially eluted are expected from a basic test or simulation. The period or the amplitude obtained through a basic test or simulation is stored in the determination unit as a determination criterion indicating that hematite has been removed. In this case, when the determination unit determines that the period or the amplitude becomes the determination criterion or less, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process, on the basis of understanding that hematite has been eluted and removed.

{0184}

Alternatively, removal of hematite may be determined from the amount of change of the period or the amplitude. In a case where hematite is substantially eluted, a difference between the amount of change of the period or the amplitude obtained in the measurement process and the amount of change of the previously obtained period or amplitude becomes gradually small. The amount of change of period change gradient or amplitude change gradient that is an inclination of period change or amplitude change per unit time is stored

in the determination unit as a determination criterion. When the determination unit determines that the amount of change of the period change gradient or the amount of change of the amplitude change gradient becomes a value within the predetermined range, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process described below, on the basis of understanding that hematite has been eluted and removed.

{0185}

Specific determination is performed according to the same idea as the method described in (1) determination based on the iron concentration in the washing liquid. When determination is made using the period or amplitude, the determination criterion is $\pm 20\%$. Further, in a case where deposition of hematite is relatively uniform in the device 10 to be washed, the determination criterion is set to $\pm 10\%$, so that determination accuracy can be improved.

{0186}

When the determination unit determines that the period or the amplitude is larger than the determination criterion, or when the determination unit determines that the amount of change of the period change gradient or the amount of change of the amplitude change gradient becomes larger than the predetermined range, the determination unit causes the control unit 104 to continue the washing process.

{0187}

Note that the chemical cleaning method of the present embodiment is also applicable to cases of using the chemical cleaning devices of the second to fourth embodiments.

{0188}

<Eighth Embodiment>

Fig. 18 is a diagram for describing a chemical cleaning device according to an eighth embodiment.

A chemical cleaning device 600 according to the eighth embodiment includes a chemical tank 601, a chemical supply line 602, a chemical discharge line 603, a control unit 604, a pump 605, a reducing atmosphere gas storage unit 611 and an air supply line 612 as a reducing atmosphere gas supply unit 610, and an exhaust line 613, similarly to the chemical cleaning device of the first embodiment. The chemical cleaning device 600 further includes a pump 606 in the chemical discharge line 603. A pressure gauge that measures a pressure of a washing liquid circulated in the chemical discharge line 603 may be installed in the chemical discharge line 603.

A chemical cleaning method according to the eighth embodiment will be described using Fig. 18. In the chemical cleaning method of the eighth embodiment, a gas supply process, a washing liquid supply process, and a discharge process are conducted, similarly to the first embodiment,

except for a washing process.

{0189}

In the washing process in the chemical cleaning method of the eighth embodiment, when a region to which hematite adheres is immersed in the washing liquid, the control unit 604 closes the pump 605 of the chemical supply line 602, and closes valves V1 and V4.

{0190}

The control unit 604 opens valves V2 and V3, and operates the pump 606. With the open of the valve V3, a reducing atmosphere gas is fed from the reducing atmosphere gas storage unit 111 to water wall tubes 13a or 13b of a once-through boiler 10 through the air supply line 112, and a gas pressure in a space above a liquid level of the washing liquid rises. At the same time, with the open of the valve V2 and the start of the pump 606, the washing liquid inside the water wall tubes 13a or 13b is fed to the chemical tank 601 through the chemical discharge line 603, and the liquid level of the washing liquid in the water wall tubes 13a or 13b is decreased.

{0191}

Next, the control unit 604 closes the valves V2 and V3 and opens the valves V1 and V4. The control unit stops the pump 606 and starts the pump 605. Accordingly, the washing liquid in the chemical tank 601 is fed to the water wall tubes

13a or 13b of the once-through boiler 10 through the chemical supply line 602, and the liquid level of the washing liquid in the water wall tubes 13a or 13b rises.

{0192}

Since pressurization of the liquid level of the washing liquid with a gas and discharge of the washing liquid using the pump are used, a flow velocity at the time of discharge of the washing liquid is higher than that of the seventh embodiment, and the washing liquid near the liquid level in the water wall tubes 13a or 13b can be more easily stirred. Therefore, detergency is further improved, compared with the seventh embodiment, and washing efficiency of hematite is increased.

{0193}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) iron concentration in the washing liquid, (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, and (4) a pressure change signal, similarly to the seventh embodiment. When a determination unit determines that hematite has been removed in the determination process, the determination unit causes the control unit 104 to terminate the washing process and to conduct a discharge process.

{0194}

The chemical cleaning device and the chemical cleaning method of the present embodiment are applicable to a case of installing a pump in a chemical discharge line in the second to fourth embodiments.

{0195}

<Ninth Embodiment>

Fig. 19 is a diagram for describing a chemical cleaning device according to a ninth embodiment.

A chemical cleaning device 700 according to the ninth embodiment includes a chemical tank 701, a chemical supply line 702, a chemical discharge line 703, a control unit 704, a pump 705, a reducing atmosphere gas storage unit 711 and an air supply line 712 as a reducing atmosphere gas supply unit 710, and an exhaust line 713, similarly to the chemical cleaning device of the first embodiment. The chemical cleaning device 700 further includes a circulation line 720.

Note that a similar circulation line can be installed to the chemical cleaning devices of the second to fourth embodiments.

{0196}

The circulation line 720 is connected to a lower header 14a or 14b as one end side of a once-through boiler, and an upper header 15a or 15b as the other end side. A circulation pump 721 is installed in a middle position of the circulation line 720. The circulation line 720 and the circulation pump

721 may be temporarily installed.

A pick-out portion 722 is installed on a downstream side of the circulation pump 721.

{0197}

A circulating direction of a washing liquid is not especially limited. In the configuration of Fig. 19, the washing liquid is circulated to distribute upward in water wall tubes 13a or 13b. However, the washing liquid may be circulated to distribute downward.

{0198}

In the present embodiment, the temperature of the washing liquid is near an environmental temperature, and a circulation flow rate may be a small flow rate that enables circulation at least one time during the washing process. Therefore, a discharge pressure of the circulation pump 721 may be low.

{0199}

A chemical cleaning method using the chemical cleaning device 700 of the ninth embodiment will be described below. In the chemical cleaning method of the ninth embodiment, a gas supply process and a discharge process are conducted, similarly to the first embodiment.

{0200}

<Washing Liquid Supply Process>

The control unit 704 starts the pump 705, and opens valves V1 and V4. The washing liquid in the chemical tank 701

is fed to a once-through boiler 10 through the chemical supply line 702. In the ninth embodiment, the washing liquid is supplied to all of the lower header, the water wall tubes, and the upper header of the once-through boiler 10, and the circulation line 720. The control unit 704 stores the amount of the washing liquid in which all of the lower header, the water wall tubes, and the upper header, and the circulation line 720 can be immersed, and feeds a predetermined amount of the washing liquid to the once-through boiler 10 in a washing liquid supply process.

{0201}

Here, a valve installed on piping that connects the once-through boiler 10 and the steam-water separator 30 is closed. In doing so, the washing liquid can be prevented from flowing into a steam-water separator 30 that is a device adjacent to the once-through boiler 10 on a downstream side.

{0202}

<Washing Process>

When the predetermined amount of the washing liquid is fed to the once-through boiler 10, the control unit 704 stops the pump 705, and closes the valves V1 and V4. Next, the control unit 704 starts the circulation pump 721. With the start of the circulation pump 721, the washing liquid passes through the lower header 14a or 14b, the water wall tubes 13a or 13b, the upper header 15a or 15a, and the circulation line

720. That is, in the present embodiment, the washing liquid is circulated without flowing into other devices (an economizer 26 and the steam-water separator 30) adjacent to the once-through boiler 10. The circulation is conducted at a flow rate that enables the washing liquid to flow at least once between the once-through boiler 10 to the circulation line 720 during the period of the washing process.

{0203}

Note that the number of rotation of the circulation pump 721 may be increased/decreased at predetermined periods. In doing so, a flow velocity of the washing liquid distributed in the water wall tubes 13a or 13b varies, and washing performance is further improved.

{0204}

Further, the temperature of the washing liquid rises when the washing liquid passes through the circulation pump 721. Therefore, the washing processing conducted at a higher temperature (to be specific, higher than an environmental temperature around the water wall tubes 13a or 13b, and the environmental temperature + 10°C, or less) than a case where the washing liquid is left to stand during the washing process like the first embodiment.

{0205}

During the washing process, the distribution path of the washing liquid (the lower header 14a or 14b, the water wall

tubes 13a or 13b, the upper header 15a or 15b, and the circulation line 720) configures a close space. Therefore, an oxidation-reduction potential of the washing liquid during the washing process is maintained from -0.8 V to -0.4 V, both inclusive (on the basis of a silver-silver chloride electrode reference).

{0206}

In the present embodiment, termination of the washing process is determined on the basis of any of (1) iron concentration in the washing liquid, (2) color change of a hematite adhering portion, and (3) an analysis result of an internal state from an outside of the water wall tube, and (4) pressure change, similarly to the first embodiment.

In the case of determination based on (1) iron concentration in the washing liquid, the washing liquid may be collected in the chemical tank 701 and the iron concentration may be measured like the first embodiment. Alternatively, a part of the washing liquid passing through the circulation line 720 may be collected through the pick-out portion 722 and may be used for measurement of the iron concentration.

{0207}

In the case of determination based on (4) pressure change, a pressure gauge is installed in the circulation line 720, similarly to the seventh embodiment. Operation to increase/decrease the number of rotation of the circulation

pump 721 by a predetermined frequency is performed, and a determination unit determines a state in which hematite is eluted and removed, on the basis of a similar idea described in the seventh embodiment, using a pressure value measured with the pressure gauge installed in the circulation line 720.

{0208}

When the determination unit determines that hematite has been removed in the determination process, the determination unit causes the control unit 104 to terminate the washing process and to conduct the discharge process.

{0209}

According to the present embodiment, a flow velocity is given to the washing liquid, the washing liquid is stirred, and further, the washing liquid is heated during the washing process. Therefore, detergency is improved, compared with the first embodiment in which no circulation line is provided, and washing efficiency of hematite is increased.

{Reference Signs List}

{0210}

- 1 Thermal power generation system
- 10, 10a, and 10b Once-through boiler
- 11a and 11b Combustion chamber
- 12a and 12b Wall surface
- 13, 13a, and 13b Water wall tube
- 14a and 14b Lower header

15a and 15b Upper header

16 Branching portion

100, 200, 300, 400, 500, 600, and 700 Chemical cleaning device

101, 201, 301, 401, 501, 601, and 701 chemical tank

102, 202, 302, 402, 502, 602, and 702 chemical supply line

103, 203, 303, 403, 503, 603, and 703 chemical discharge line

104, 204, 304, 404, 504, 604, and 704 Control unit

105, 205, 305, 405, 505, 605, 606, and 705 Pump

110, 210, 410, 510, 610, and 710 Reducing atmosphere gas supply unit

111, 411, 511, 611, and 711 Reducing atmosphere gas storage unit

112, 412, 512, 612, and 712 Air supply line

113, 213, 413, 513, 613, and 713 Exhaust line

120 Cut test piece

121 Transparent plate

122 Space

130 By-pass portion

131 By-pass pipe

132 Tubular test piece

140 Current characteristic evaluation device

150 Pressure gauge

310 Reducing atmosphere regulator supply unit

311 Reducing atmosphere regulator storage unit

- 312 Reducing atmosphere regulator supply line
- 406 Circulation loop
- 520 Water supply unit
- 521 Water tank
- 522 Water supply line
- 523 Water filling pump
- 720 Circulation line
- 721 Circulation pump
- 722 Pick-out portion

{CLAIMS}

{Claim 1}

A chemical cleaning method comprising:

a washing liquid supply process of supplying a washing liquid containing a rust removing agent that is a chelating agent, a reducing agent, or a mixture of the chelating agent and the reducing agent, to a device to be washed including a member to which hematite adheres; and

a washing process of immersing at least a region to which the hematite adheres in the member into the washing liquid, maintaining an oxidation-reduction potential of the washing liquid at a value at which the hematite is eluted into the washing liquid, and removing the hematite from the member, wherein

the chelating agent is any one of an aminocarboxylic acid-based chelating agent, an oxycarbonic acid-based chelating agent, and an organic phosphorus-based chelating agent,

the reducing agent is any one of a metal ion, sulfite, an oxalic acid, a formic acid, an ascorbic acid, pyrogallol, hydrazine, and hydrogen, and

pH of the washing liquid falls within a range of 4 to 8.

{Claim 2}

The chemical cleaning method according to claim 1, wherein

the value is maintained within a range from -0.8 V to -0.4 V, both inclusive, on a basis of a silver-silver chloride electrode reference, and the washing process is conducted.

{Claim 3}

The chemical cleaning method according to claim 1 or 2, wherein

the value is adjusted by supplying a reducing atmosphere gas to the device to be washed.

{Claim 4}

The chemical cleaning method according to any one of claims 1 to 3, wherein

a temperature of the washing liquid during the washing process falls within a range from an environmental temperature around the member to a temperature higher than the environmental temperature by 10°C, both inclusive.

{Claim 5}

The chemical cleaning method according to any one of claims 1 to 4, wherein

the region is immersed in the washing liquid in a state where the washing liquid is left to stand.

{Claim 6}

The chemical cleaning method according to any one of claims 1 to 4, wherein

a process of discharging the washing liquid from the member and a process of feeding the discharged washing liquid

to the member are repeated, and a height of a liquid level of the washing liquid is moved near the region, during the washing process.

{Claim 7}

The chemical cleaning method according to any one of claims 1 to 4, wherein

the washing liquid passes through the member and is discharged from an upstream-side end portion of the member, and the discharged washing liquid is directly circulated into a downstream-side end portion of the member, during the washing process.

{Claim 8}

The chemical cleaning method according to any one of claims 1 to 4, further comprising:

a measurement process of measuring iron concentration in the washing liquid; and

a determination process of determining a removal state of the hematite from the member on a basis of the iron concentration, wherein

the washing liquid is discharged from the device to be washed during the washing process, and the iron concentration in the discharged washing liquid discharged in the measurement process is measured, and,

when the iron concentration is determined to be predetermined concentration or more, or when an amount of

change of concentration gradient is determined to be a value within a predetermined range, in the determination process, the washing process is terminated.

{Claim 9}

A chemical cleaning device for performing chemical cleaning of a device to be washed including a member to which hematite scale adheres, the chemical cleaning device comprising:

a chemical tank adapted to accommodate a washing liquid containing a rust removing agent that is a chelating agent, a reducing agent, or a mixture of the chelating agent and the reducing agent, and having pH falling within a range of 4 to 8, the chelating agent being any one of an aminocarboxylic acid-based chelating agent, an oxycarbonic acid-based chelating agent, and an organic phosphorus-based chelating agent, and the reducing agent being any one of a metal ion, sulfite, an oxalic acid, a formic acid, an ascorbic acid, pyrogallol, hydrazine, and hydrogen;

a chemical supply line connecting the device to be washed and the chemical tank, and adapted to supply the washing liquid to the member;

a pump installed in the chemical supply line;

a chemical discharge line connecting the device to be washed and the chemical tank, and adapted to discharge the washing liquid from the member;

a means adapted to immerse at least a region to which the hematite adheres in the member into the washing liquid; and

a means adapted to maintain an oxidation-reduction potential of the washing liquid during washing at a value at which the hematite is eluted into the washing liquid, wherein

the chemical tank, the chemical supply line, and the pump are means to supply the washing liquid to the member.

{Claim 10}

The chemical cleaning device according to claim 9, further comprising:

a reducing atmosphere adjustment unit adapted to adjust the value to a value within a range from -0.8 V to -0.4 V , both inclusive, on a basis of a silver-silver chloride electrode reference.

{Claim 11}

The chemical cleaning device according to claim 9 or 10, wherein

the reducing atmosphere adjustment unit supplies a reducing atmosphere gas to the device to be washed.

{Claim 12}

The chemical cleaning device according to any one of claims 9 to 11, wherein

a temperature of the washing liquid supplied to the member falls within a range from an environmental temperature around the member to a temperature higher than the

environmental temperature by 10°C, both inclusive.

{Claim 13}

The chemical cleaning device according to any one of claims 9 to 12, further comprising:

a circulation loop connecting the chemical supply line on an upstream side and the chemical supply line on a downstream side across the pump, wherein

a part of the washing liquid having passed through the pump is conveyed to the upstream side of the pump through the circulation loop.

{Claim 14}

The chemical cleaning device according to any one of claims 9 to 13, wherein

supply of the washing liquid to the member and discharge of the washing liquid from the member are stopped, and the washing liquid is left to stand, during washing.

{Claim 15}

The chemical cleaning device according to any one of claims 9 to 14, further comprising a water supply unit that comprises:

a water tank adapted to accommodate water;

a water supply line connecting the water tank and the device to be washed; and

a water filling pump installed in the water supply line.

{Claim 16}

The chemical cleaning device according to any one of claims 9 to 12, wherein

discharge of the washing liquid in the member toward the chemical tank through the chemical discharge line, and feed of the washing liquid in the chemical tank to the member through the chemical supply line are repeated during washing.

{Claim 17}

The chemical cleaning device according to any one of claims 9 to 12, further comprising:

a circulation unit including a circulation line connecting an upstream-side end portion and a downstream-side end portion of the member, and a circulation pump installed in the circulation line, wherein

the washing liquid discharged from the downstream-side end portion is circulated to the upstream-side end portion through the circulation line during washing.

{Claim 18}

The chemical cleaning device according to any one of claims 9 to 12, further comprising:

a determination unit adapted to determine a removal state in which the hematite from the member is eluted on a basis of iron concentration in the washing liquid discharged from the device to be washed, while an oxidation-reduction potential of the washing liquid of the device to be washed is maintained at a value at which the hematite is eluted into the washing

liquid, and the device to be washed is being washed, and adapted to terminate the washing of the device to be washed when the determination unit determines that the iron concentration is predetermined concentration or more, or when the determination unit determines that an amount of change of concentration gradient is a value within a predetermined range.