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(54) **Eljárás lerakódások megakadályozására hűtővízkörökben**

Method for preventing deposits in cooling water circuits

The present invention relates to a method for preventing deposits in cooling water circuits, in which cooling water is fed from a process heat exchanger to a cooling tower, there cooled in contact with ambient air and drained into a collecting tank and then fed back to the process heat exchanger, wherein the pH of the cooling water is recorded continuously or at regular intervals at a first measuring site and, depending on the difference between the pH recorded at the first measuring site and a predetermined first target value, carbon dioxide is fed to the cooling water, wherein the carbon dioxide is fed upstream of the process heat exchanger, but downstream of the cooling tower and the pH is recorded at the first measuring site downstream of the process heat exchanger, but upstream of the cooling tower.

In the operation of open cooling systems, mineral deposits form which consist, for example, of lime, calcium sulphate, calcium phosphate, magnesium hydroxide, magnesium silicate, magnesium carbonate or iron compounds or silicon compounds. Such deposits precipitate out of the cooling water during operation and adhere to the pipes of the cooling system and to the packing of the cooling tower. To prevent these deposits, a considerable cleaning effort is necessary; frequently, entire pipe sections must be replaced.

Therefore it has been and is being attempted to counteract the formation of such deposits by influencing the chemical composition of the cooling water.

An important factor in this case is the pH of the cooling water. If this exceeds a value of pH=8.3, the concentration of CO_3 ions increases greatly, which promotes the formation of lime deposits. If, in contrast, the pH falls below the value of pH=4.3, the concentration of HCO_3 ions falls, as a result of which the risk of corrosion of pipes and other parts of the cooling water circuit increases.

For pH control, first the addition of mineral acids is suggested, such as, for example, HCl or H_2SO_4. The use of mineral acids, however, is not without problems, since the handling thereof is not risk-free, and furthermore said acids can cause corrosion on the circuit pipes. In addition, in the case of increasing concentration, the elevated salt concentrations in the blowdown water (=bleed off) are frequently problematic and relevant to official approvals.

In contrast, the use of carbon dioxide for pH control in cooling water circuits has proved itself. In the absence of water, carbon dioxide is inert and noncorrosive. In contrast to mineral acids, it is safe to handle, environmentally friendly, simple in metering and protects the cooling water circuit against overacidification. In the case of use of CO_2 in cooling water circuits, even at relatively high concentrations, the salt content does not increase disproportionately and the alkalinity in the water remains constant or is even slightly increased; both aspects are important for favourable chemical corrosion properties of the cooling water. Examples of systems that work with carbon dioxide may be found, for instance, in US 4 547 294 A1 and in FR 2 801 300 A1. There, methods are described for preventing mineral deposits, such as boiler scale, etc., in cooling circuits, in which carbon dioxide is added to the cooling water to control the pH. Using the methods described there, the pH in the entire cooling water circuit is intended to be kept at pH ≈ 7.5, or between pH = 7.9 and pH = 8.4.

In EP 2 213 630 A1 or US 2013 0 026 105 A1, likewise methods are described for preventing the formation of deposits in cooling circuits. Here, various parameters that are relevant to the formation of deposits, such as pH, alkalinity, concentration of Ca^{2+} ions, etc. are measured and used to calculate a target value for the

pH, wherein specific hardness indices, such as, for example, the Langelier saturation index (LSI) or the Ryznar stability index (RSI) are taken into account. By means of the controlled addition of carbon dioxide to the cooling water circuit, the pH of the cooling water is then brought to the calculated target value.

Using carbon dioxide, the pH of the cooling water in the pipes of the cooling water circuit can be readily controlled; however, the carbon dioxide, on contact with air in the cooling tower, is, to a not inconsiderable amount, taken off from the cooling water and removed from the cooling water circuit by the cooling air ("CO2 stripping"). As a result, at the same time the pH of the cooling water increases in a collecting tank downstream of the cooling tower. There is therefore a considerable difference between the pH of the cooling water fed to the cooling tower and the significantly higher pH of the cooling water in the collecting tank, with the consequence that, in the cooling tower and the connecting pipe sections of the cooling water circuit, the risk of formation of lime deposits and other deposits increases. The extent to which the carbon dioxide is taken off from the cooling water is dependent on various circumstances and can only be controlled with difficulty.

It is therefore the object of the present invention to provide a method for preventing lime deposits and other deposits in cooling circuits, with the use of carbon dioxide, in which the pH in the entire cooling water circuit is kept at a value at which the formation of alkaline deposits is likewise reliably prevented, as is the corrosion of pipe sections.

This object is achieved according to the invention in that, in the cooling water circuit, upstream of the feed of the carbon dioxide, the pH of the cooling water is recorded at a second measuring site, and, depending on the difference between the pH recorded at the second measuring site and a predetermined second target value, a mineral acid is fed to the cooling water, wherein the controls of the addition of carbon dioxide and of the mineral acid proceed independently of one another.

According to the invention, therefore, there is a double measurement of the pH within the cooling water circuit at different measuring sites, each of which, independently of one another, are used as starting factor for controlling a pH in the cooling water circuit. By the addition of the mineral acid, the pH of the cooling water is reduced in the entire cooling water circuit, the addition of the carbon dioxide ensures an optimization of the pH in the pipe sections of the cooling water circuit upstream of the cooling tower. Since the mineral acid present in the cooling water is not subjected to the stripping process in the cooling tower, as the carbon dioxide is, it ensures a substantially uniform depression of the pH in the cooling water in the entire cooling water circuit; in particular, it ensures, in the region of the cooling tower packing, a pH at which both the formation of deposits in this region and corrosion processes are avoided as far as possible.

By means of the controls that are independent of one another of the addition of carbon dioxide and a mineral acid, the pH in the entire cooling water circuit is kept within a range in which firstly the formation of lime deposits and other deposits, such as, for example, deposits of calcium sulphate, calcium phosphate, magnesium hydroxide, magnesium silicate, magnesium carbonate or iron compounds or silicon compounds, and also secondly the risk of corrosion, are minimized. By controlling the pH by means of the addition of mineral acid, in particular, the risk of formation of deposits in the region of the cooling tower packing as a consequence of the "CO_2 stripping" is prevented. In this case, it is not important at what point in the cooling water circuit the mineral acid is fed; in particular, it is not necessary to introduce the mineral acid directly into the collecting tank or into the fresh water that is fed to the cooling water circuit. Since the mineral acid is distributed in the entire

cooling water circuit, the pH in the entire system is reduced at least to the pH of the second target value. The further reduction of the pH by feeding carbon dioxide additionally safeguards the system against the risk of formation of deposits, in particular in the sections downstream of the process heat exchanger, in which the cooling water is conveyed at elevated temperatures.

An advantageous development of the invention provides that the second target value of the pH is greater than the first target value of the pH of the cooling water. By adding the mineral acid, the pH of the cooling water is brought to a range of for example pH < 8.3, at which the formation of said deposits is already substantially suppressed. By adding the carbon dioxide, the pH of the cooling water is further optimized; in particular as a result, the shifting of the optimum pH by the temperature elevation in the process heat exchanger is taken into account. The second measuring site for the pH is upstream of the feed-in site for the carbon dioxide and downstream of the cooling tower; preferably, it is in the region of the collecting tank. The first target value is selected in such a manner that firstly deposits, and secondly, corrosion phenomena, on the pipes owing to the carbon dioxide input are reduced to a minimum.

Preferably, as a first target value for the pH in the cooling water, pH ≥ 7.0, particularly preferably pH ≥ 7.5 is chosen. However, at the same time, it should not exceed a maximum value in order to ensure that the formation of deposits in the region already above the feed-in point for the carbon dioxide into the cooling water circuit is substantially suppressed. The second target value should be selected to be higher than the first target value, and in this case not exceed a defined maximum value which depends on the chemical and physical properties of the cooling water and on whether and to what extent further chemicals such as, e.g., antiscalants or corrosion inhibitors are added to the cooling water. For example, this maximum value is between pH=8.0 and pH=8.3.

Another advantageous embodiment of the invention is characterized in that chemical or physical parameters of the cooling water are measured and used for determining the first target value or the second target value. "Chemical parameters" are here taken to mean, in particular, properties by dissolved components of the water such as, for example, the total dissolved salts (TDS) in the cooling water, the concentration of certain ions, such as Ca^{2+}, PO_4^{3+}, SO_3^{2-}, SiO_4, polymers, etc., or the alkalinity of the cooling water. "Physical parameters" are taken to mean physical properties such as, for example, the temperature of the cooling water at various points in the cooling water circuit, or the ambient pressure. Depending on the measured chemical and physical parameters, then, a target value for the pH or a pH range is determined, which, under the respective conditions, leads to the lowest possible tendency of formation of deposits, firstly, and formation of corrosion on the pipes in the cooling water circuit, secondly. To calculate the target value, recording and evaluation systems can also be used such as are offered by various manufacturers, for example the system distributed by Nalco under the name "3D TRASAR®". In particular, the measured chemical or physical parameters can also be used to determine hardness indices such as, for example, the Langelier saturation index (LSI) or the Ryznar stability index (RSI) and to calculate therefrom the target value for the pH. In the case of the Langelier saturation index, the pH at the first measuring site, for example, is adjusted in such a manner that one of the following inequalities is met:

-0.3 < LSI < 0.3, if no antiscalants are added to the cooling water,

-0.3 < LSI < 1.5 if antiscalants are fed to the cooling water.

In the relevant methods for determining a target value, however, the solubilities of other substances, for example calcium sulphate, calcium phosphate, magnesium hydroxide, silica or magnesium silicate, and also the corrosion risks of the materials in the cooling circuit that are used are also taken into consideration.

The carbon dioxide is fed according to the invention in the cooling water circuit upstream of the process heat exchanger, but downstream of the cooling tower. This is intended, in particular, to counteract the risk that when the cooling water is heated during the passage through the process heat exchanger, there is precipitation of salts and thereby formation of deposits in the process heat exchanger or the pipe sections of the cooling water circuit running downstream thereof. For example, the feed proceeds directly in the collecting tank or in a pipe section downstream of the collecting tank. In order to ensure clear separation of the two control circuits of carbon dioxide and mineral acid, it is advantageous but admittedly not absolutely necessary, to feed the carbon dioxide downstream of a pump arranged in the cooling water circuit, whereas the mineral acid is fed upstream of this pump.

According to the invention, the pH is recorded at the first measuring site in the cooling water circuit downstream of the process heat exchanger, but upstream of the cooling tower. In the control of the carbon dioxide feed, the change of the water temperature after passage through the process heat exchanger is taken into account thereby.

The method according to the invention can proceed with or without the feed of further chemicals into the cooling water such as, for example, polymer-based antiscalants, or corrosion inhibitors.

Preferably, the carbon dioxide is fed to the cooling water under pressure in the liquefied state and is expanded on introduction into the cooling water, as a result of which efficient dissolution of the carbon dioxide in the cooling water occurs. Alternatively, or as a supplement thereto, the carbon dioxide, however, can also be introduced in the gaseous form into the cooling water.

Expediently, the carbon dioxide is withdrawn from a tank for liquid or gaseous carbon dioxide, a cylinder or a carbon dioxide line to which the cooling water circuit is connected. The use of carbon dioxide from off-gas is particularly advantageous.

An exemplary embodiment of the invention is to be explained in more detail with reference to the drawing. The sole drawing (Fig. 1) shows schematically a cooling water circuit operating according to the invention.

The cooling water circuit 1 shown in Fig. 1 comprises a cooling tower 2 with collecting tank 3 that is intended for collecting the cooling water draining from the cooling tower 2. A pump 5 and also a process heat exchanger 6 are integrated into a circuit pipe 4 proceeding from the collecting tank 3 and opening out into the cooling tower 2. The process heat exchanger 6 is, for example, a single heat exchanger or a system of a plurality of parallel- or series-connected heat exchangers in which the cooling water conducted in the circuit pipe comes into heat exchange with a process medium and is heated in the course of this. In addition, a fresh water feed pipe 7 and also a bleed-off pipe 8 open out into the collecting tank 3. Via the bleed-off pipe 8, part of the cooling water is taken off in order to avoid excessive concentration of salts in the cooling water. The fresh water feed pipe 7 serves for replacing cooling water that is removed into the ambient atmosphere in the cooling process in the cooling tower 2 or has been taken off from the cooling water circuit 1 by withdrawal via the bleed-off pipe 8.

In the cooling water circuit 1 shown in Fig. 1, the pH of the cooling water is controlled at two different sites. A first control circuit 10 comprises a first measuring site 11 for recording the pH, which first measuring site is arranged upstream of the cooling tower 2, in the exemplary embodiment immediately upstream of the junction of the circuit pipe 4 with the cooling tower 2. The arrangement shown in the exemplary embodiment of the measuring site 11 downstream of the process heat exchanger 6 is an advantageous solution in the context of the invention, but is not an absolutely necessary solution. The first control circuit 10 comprises, in addition, a carbon dioxide feed pipe 13 that is attached to a tank 12 for carbon dioxide, which carbon dioxide feed pipe is equipped with an electronically actuable control valve 14. The carbon dioxide feed pipe 13 opens out into the circuit pipe 4 downstream of the collecting tank 3 and the pump 5, but upstream of the process heat exchanger 6. The control valve 14 and the measuring site 11 are data-connected to an electronic control unit 15 which permits the control of the pH of the cooling water by addition of carbon dioxide depending on the pH measured at the measuring site 11 according to a stored program. Optionally, the control unit 15 is data-connected to a further measuring site 16. The measuring site 16 comprises one or more probes by means of which those properties of the cooling water are recorded that are of importance for the formation of deposits or for corrosivity, for example temperature, concentration of certain substances dissolved in the water, such as $CaCO_3$, $CaSO_4$, $Ca_3(PO_4)_2$, $Mg(OH)_2$, total dissolved salts (TDS), etc. By means of suitable calculation methods familiar to those skilled in the art, the measured values of such properties can be used to determine a pH target value which is an optimum in respect of a lowest possible tendency to formation of deposits, or of corrosion, on pipes of the cooling water circuit 1.

A second control circuit 20 which is arranged upstream of the control circuit 10 in the cooling water circuit 1 comprises a second measuring site 21 for recording the pH in the cooling water. The second measuring site 21 is arranged upstream of the junction of the carbon dioxide pipe 13 on the circuit pipe 4 and of the pump 5. The second control circuit 20 comprises, in addition, a storage container 22 for a mineral acid, in the exemplary embodiment sulphuric acid. From the storage container 22, a mineral acid feed pipe 23 departs, which opens out into the cooling water circuit 1. In the exemplary embodiment, the mineral acid feed pipe 23 opens out into the collecting tank 3 in parallel to the fresh water feed pipe 7, but the mineral acid pipe can open out into the circuit pipe 4 at any other desired site. In the mineral acid feed pipe 23, a conveying appliance 24 is integrated, which is equipped with an electronically controllable motor. The motor of the conveying appliance 24 and the measuring site 21 are data-connected to an electronic control unit 25 which permits the control of the pH of the cooling water by addition of mineral acid, depending on the measured pH according to a stored program.

When the cooling water circuit 1 is in operation, in the control circuit 10 the pH recorded at the measuring site 11 is controlled to a predetermined target value. In this case the pH at the measuring site 11 is recorded continuously or at regular time intervals and passed to the control unit 15. In the control unit 15 a target value is stored for the pH (hereinafter also called "first target value"), which is selected in such a manner that firstly, depending on the conditions existing in the cooling water, a tendency that is as low as possible to formation of lime deposits and other deposits exists, and secondly no acid-caused corrosion occurs on the pipes of the cooling water circuit 1. As an alternative to a fixed predetermined target value, the first target value can also be calculated continuously in a manner familiar to those skilled in the art, wherein, for this purpose, the parameters measured at measuring site 16 are included. Corresponding to the difference between the pH

measured at the measuring site 11 and the first target value, the control unit 15 sends a signal to the control valve 14 in order to feed carbon dioxide from the tank 12 into the circuit pipe or to block the feed of carbon dioxide.

In the control circuit 20, a further control of the pH in the cooling water proceeds. For this purpose, the pH at the measuring site 21 is recorded continuously or at predetermined time intervals, and passed to the control unit 25. In the control unit a target value for the pH (hereinafter also called "second target value") is stored. Depending on the difference between the second target value and the pH recorded at the measuring site 21, the control unit 25 sends a corresponding control signal to the conveying appliance 24 in order to add mineral acid from the storage container 22 to the cooling water circuit 1 or to block the feed of mineral acid. The pH target value of the control circuit 20 in this case is always higher than the target value of the control circuit 10 and preferably selected in such a manner that, for the first target value in control circuit 10, a value of $pH \geq 7.0$, preferably $pH \geq 7.5$ can be selected. For example, the second target value is between pH = 7.8 and pH = 8.3, and the first target value is pH = 7.6.

Since the carbon dioxide fed to the cooling water via the carbon dioxide feed pipe 13 escapes again at least in part from the cooling water during passage through the cooling tower 2 and the cooling water dripping from the cooling tower 2 into the collecting tank 3 has in this respect a higher pH than the cooling water fed to the cooling tower 2, the addition of the mineral acid achieves, in particular, the pH in the cooling tower 2 being reduced to a value at which the formation of deposits in the cooling tower packing is at least substantially prevented.

With the method according to the invention, both the formation of lime deposits and other deposits and also corrosion in the pipe system are avoided, and the losses of carbon dioxide in the cooling tower are markedly reduced. At the same time, the known advantages of CO_2 as means for controlling the pH are utilized.

List of reference signs

1	Cooling water circuit
2	Cooling tower
3	Collecting tank
4	Circuit pipe
5	Pump
6	Heat exchanger
7	Fresh water feed pipe
8	Bleed-off pipe
9	-
10	Control circuit
11	Measuring site
12	Tank
13	Carbon dioxide feed pipe
14	Control valve
15	Control unit
16	Measuring site
17	-
18	-
19	-
20	Control circuit
21	Measuring site
22	Storage container
23	Mineral acid feed pipe
24	Conveying appliance
25	Control unit

ELJÁRÁS LERAKÓDÁSOK MEGAKADÁLYOZÁSÁRA HŰTŐVÍZKÖRÖKBEN

Szabadalmi igénypontok

1. Eljárás lerakódások megakadályozására nyitott hűtővízkörökben, amelynél hűtővizet folyamathőcserélőből (6) hűtőtoronyba (2) vezetünk, ott környezeti levegővel érintkeztetve lehűtünk és gyűjtőmedencébe (3) csepegtetünk, majd végezetül a folyamathőcserélőbe (6) visszavezetünk, ahol a hűtővíz pH-értékét első mérési helyen (11) folyamatosan vagy szabályos időközönként megmérjük, továbbá az első mérési helyen (11) mért pH-érték és egy előre meghatározott első célérték közötti különbségtől függően a hűtővízhez szén-dioxidot adunk,

ahol a szén-dioxid hozzáadását áramlásirányban a folyamathőcserélő (6) előtt, de áramlásirányban a hűtőtorony (2) után hajtjuk végre, és a pH-érték első mérési helyen (11) történő mérését áramlásirányban a folyamathőcserélő (6) után, de áramlásirányban a hűtőtorony (2) előtt hajtjuk végre,

azzal jellemezve, hogy

a hűtővízkörben a hűtővíz pH-értékét áramlásirányban a szén-dioxid hozzáadása előtt és áramlásirányban a hűtőtorony (2) után második mérési helyen (21) megmérjük, továbbá a második mérési helyen (21) mért pH-érték és egy előre meghatározott második célérték közötti különbségtől függően a hűtővízhez ásványi savat adunk, ahol a szén-dioxid és az ásványi sav hozzáadásának szabályozását egymástól függetlenül végezzük.

2. Az 1. igénypont szerinti eljárás, **azzal jellemezve**, hogy a hűtővíz pH-értékének második célértéke a pH-érték első célértékét meghaladó nagyságú.

3. Az 1. vagy a 2. igénypont szerinti eljárás, **azzal jellemezve**, hogy a pH-érték első célértékének a hűtővízben pH>7,0 értéket, előnyösen pH>7,5 értéket választunk.

4. Az előző igénypontok bármelyike szerinti eljárás, **azzal jellemezve**, hogy a hűtővíz kémiai vagy fizikai paramétereit megmérjük és az első célérték vagy a második célérték meghatározására használjuk.

5. Az előző igénypontok bármelyike szerinti eljárás, **azzal jellemezve**, hogy a hűtővízhez további vegyszereket, például vízkő elleni szereket vagy korróziógátló szereket adunk.

6. Az előző igénypontok bármelyike szerinti eljárás, **azzal jellemezve**, hogy a szén-dioxidot a hűtővízhez folyékony vagy gáz halmazállapotban adjuk hozzá.

7. Az előző igénypontok bármelyike szerinti eljárás, **azzal jellemezve**, hogy a szén-dioxidot tartályból, palackból, széndioxid-vezetékből vagy füstgázforrásból nyerjük.

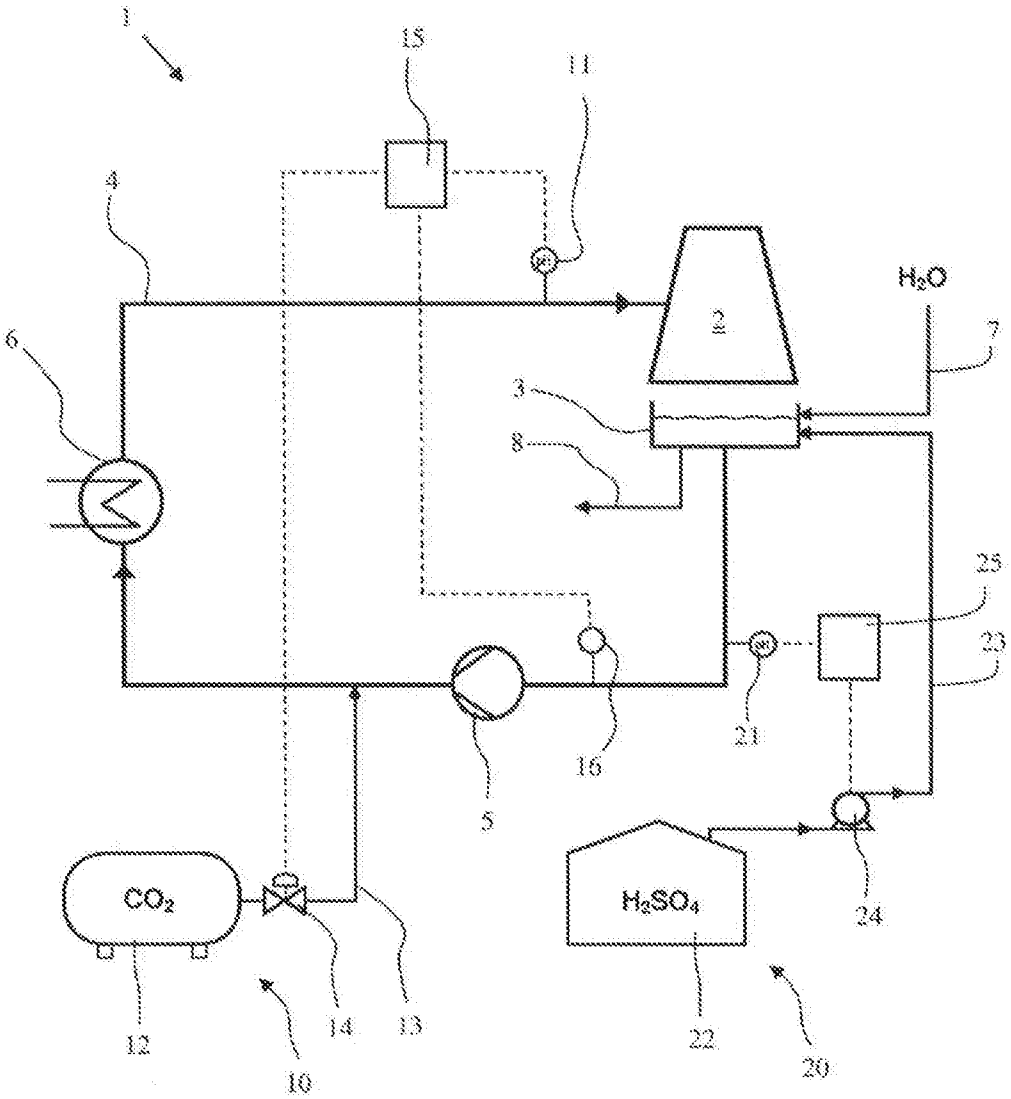

Fig. 1