

Method for treating a cooling water system

Field of Invention

[0001]

The present invention relates to a method for treating a cooling water system for forming an anticorrosive film on the surface of a metal member of the cooling water system.

Background of Invention

[0002]

Iron based metals used for a material of members of a recirculating cooling water system such as a heat tube and piping corrode when they are kept in contact with water. There is a method for preventing corrosion of the iron based metal members by forming a thin anticorrosive film on the surface of the members by adding various corrosion inhibitors to the cooling water system.

[0003]

The method for preventing corrosion includes an initial treatment process performed when the recirculating cooling water system starts to operate, and a normal treatment process performed during a normal operation of the recirculating cooling water system after the initial treatment process is performed.

[0004]

An anticorrosive film is not usually formed on the surface of a metal member in the beginning when the recirculating cooling water system starts to operate, and thus the metal members are exposed to a heavily corrosive condition. A corrosion inhibitor is added to the recirculating cooling water system at a relatively high concentration to form an anticorrosive film on the surface of the iron based metal members during the initial

treatment process.

[0005]

During the normal treatment process, a corrosion inhibitor is added to the recirculating cooling water system at a low concentration to maintain the anticorrosive film formed on the surface of the iron based metal members during the initial treatment process.

[0006]

As for the conventional initial treatment process performed in the beginning of the operation of the recirculating cooling water system, there is a method for forming an anticorrosive film on the surface of the iron based metal members by adding an inorganic phosphate and a zinc compound to the cooling water, and then circulating the cooling water for a certain period of time.

[0007]

The anticorrosive film thus formed has a double-layered structure consisting of a fine or dense base layer mainly composed of iron phosphate and iron oxide, and a fine surface layer mainly composed of zinc phosphate. The fine anticorrosive film having the double-layered structure has a function of anodic protection and cathodic protection and thus prevents corrosion of the iron based metal members (JP2003-105573A).

[0008]

JP2003-105573A discloses in its 0037 paragraph a method in which the initial treatment process is performed under the conditions of a calcium hardness of 120 mg CaCO_3/L , a zinc ion concentration of 0.13 mmol/L, a sodium hexametaphosphate

concentration expressed as a phosphorus atom concentration of 1.58 mmol/L, and a pH of 7.0. It discloses in its 0045 paragraph another method in which the initial treatment process is performed under the conditions of a calcium hardness of 240 mg CaCO₃/L, a zinc ion concentration of 0.13 mmol/L, a sodium hexametaphosphate concentration expressed as a phosphorus atom concentration of 3.16 mmol/L, and a pH of 7.0.

[0009]

JP2005-290419A discloses in its 0004 paragraph a method for forming an initial anticorrosive film using a phosphate and a zinc compound.

List of Prior Art Documents

Patent Documents

[0010]

Patent Document 1: JP2003-105573A

Patent Document 2: JP2005-290419A

Object and Summary of Invention

[0011]

It is an object of the present invention to provide a method for treating a cooling water system capable of forming an anticorrosive film having improved anticorrosive effects during the initial treatment process.

[0012]

A first aspect of the present invention provides a method for treating a cooling water system comprising an initial treatment process for forming an initial anticorrosive film on the surface of a metal member of the cooling water system by adding a phosphate and a zinc compound to the cooling water system when the

cooling water system starts to operate. The initial treatment process has a primary initial treatment process and a secondary initial treatment process. The primary initial treatment process is performed for 5 to 36 hours under the conditions of a total phosphate concentration of 70 to 120 mg PO_4/L , a zinc concentration of 10 to 30 mg Zn/L , a calcium hardness of 25 to 75 mg CaCO_3/L , and a pH of 6.0 or higher and lower than 7.0. The secondary initial treatment process is performed under the condition of a pH of 7.0 to 7.5.

[0013]

According to a second aspect, the primary initial treatment process is performed for 5 to 24 hours in the first aspect.

[0014]

According to a third aspect, the calcium hardness is maintained at 40 to 60 mg CaCO_3/L during the primary initial treatment process in the first or second aspect.

Advantageous Effects of the Invention

[0015]

An anticorrosive film having improved anticorrosive effects is formed according to the present invention. The mechanism thereof is not fully clear but surmised as follows:

[0016]

During the initial treatment process in the method for treating a cooling water system of the present invention, iron ions are dissolved in the cooling water system from iron based metal members thereof by anodic corrosion reaction, and the iron ions react with phosphate ions in the water to form iron

phosphate. In addition, OH^- ions are produced by cathodic corrosion reaction, and the OH^- ions react with zinc ions to form zinc hydroxide. Under the conditions of the primary initial treatment process in the method of the present invention, the iron phosphate and the zinc hydroxide are produced efficiently, and thus a dense anticorrosive film involving them is formed. After the primary initial treatment process, the secondary initial treatment process is performed at a pH of 7.0 to 7.5. During the secondary initial treatment process, calcium ions in the water react with the phosphate ions to form calcium phosphate, thereby an additional film is formed on the anticorrosive film and thus the anticorrosive film is totally strengthened.

Brief Description of Drawings

[0017]

Fig.1 is a graph showing results of experiments.

Fig.2 is a schematic figure showing experiment process.

Fig.3 is a graph showing results of experiments.

Fig.4 is a diagram of a cooling water system used in Example and Comparative Example.

Detailed Description

[0018]

The present invention is described in more detail herebelow.

[0019]

In the present invention, the primary initial treatment process is performed for 5 to 36 hours under the conditions of a total phosphate concentration of 70 to 120 mg PO_4/L , a zinc concentration of 10 to 30 mg Zn/L , a calcium hardness of 25 to 75

mg CaCO_3/L , and a pH of 6.0 or higher and lower than 7.0, and then the secondary initial treatment process is performed at a pH of 7.0 to 7.5 whereby the anticorrosive film is formed on the surface of the metal members of the cooling water system.

[0020]

The metal member is preferably iron based metal member, more preferably carbon steel member. The cooling water system is preferably an open recirculating cooling water system.

[0021]

In the cooling water system to be applied with the method of the present invention, the recirculating water preferably has a calcium hardness of 25 to 75 mg CaCO_3/L , more preferably 40 to 60 mg CaCO_3/L . When the calcium hardness is lower than 25 mg CaCO_3/L , it is difficult to form the sufficient anticorrosive film consisting of the phosphorus compound and the calcium compound formed by the action of phosphate and calcium. When the calcium hardness is higher than 75mg CaCO_3/L , deposition and adhesion of scales composed of phosphorus compound and calcium compound may be formed. When the calcium hardness of the cooling water system to be treated is outside the above range, the calcium hardness is preferably adjusted by adding a calcium hardness component such as calcium nitrate and calcium chloride to the cooling water system or by removing the calcium hardness component from the cooling water system.

[0022]

A phosphate-based corrosion inhibitor such as a phosphate and/or its salt is added to the cooling water system in such a manner that the total phosphate concentration of the cooling water

system becomes 70 to 120 mg PO_4/L , preferably 80 to 110 mg PO_4/L after addition of the corrosion inhibitor. When the phosphate concentration after addition of the corrosion inhibitor is less than 70 mg PO_4/L , it is difficult to form the sufficient anticorrosive film. When the phosphate concentration after addition of the corrosion inhibitor is higher than 120 mg PO_4/L , the phosphate concentration is too high, thereby raising concerns about the environment. When the phosphate concentration becomes lower than the above range due to consumption of the anticorrosive components during the initial treatment process, a phosphate or the like is preferably added to satisfy the range.

[0023]

Examples of the phosphate-based corrosion inhibitor include phosphate and/or its salt, specifically sodium phosphate, potassium phosphate, disodium hydrogen phosphate, dipotassium hydrogen phosphate, sodium dihydrogen phosphate and potassium dihydrogen phosphate, polymer phosphate such as pyrophosphate, tripolyphosphate and hexametaphosphate, alkali metal pyrophosphate such as potassium pyrophosphate and sodium pyrophosphate, and dihydrogen pyrophosphate such as sodium dihydrogen pyrophosphate. These may be used alone or in combination of two or more.

[0024]

Examples of the zinc compound include zinc chloride and zinc sulfate. An additive amount of the zinc compound is 10 to 30 mg Zn/L , preferably 15 to 25 mg Zn/L . In the present invention, the phosphate-based or zinc-based corrosion inhibitor is added to the cooling water system and the initial pH is adjusted to 6.0 or higher and lower than 7.0, preferably 6.0 to 6.5. When the initial

pH is 7 or higher, the amount of iron dissolved from the iron based metal member decreases, thereby the amount of iron phosphate as an ingredient for the anticorrosive film formed on the surface of the iron based metal members becomes insufficient. When the initial pH is lower than 6, the corrosivity becomes stronger, thereby raising concerns about temporary progression of corrosion of the metals to be treated and other metal materials existing in the cooling water system. It is preferable that the initial pH is adjusted by adding an acid such as hydrochloric acid or sulfuric acid, but the method for adjusting the initial pH is not limited thereto.

[0025]

In the present invention, M alkalinity of the cooling water system after the corrosion inhibitor is added and the initial pH is adjusted to 6 or higher and lower than 7 is preferable to be 10 mg CaCO_3 or higher and lower than 20 mg CaCO_3 .

[0026]

The initial treatment process is usually conducted at an ordinary temperature. When a hot area arises under a certain condition (for example, when the process for forming the initial anticorrosive film is performed while operating a heat exchanger), a polyelectrolyte having effects in preventing deposition and/or adhesion of calcium phosphate-based scales may be added if necessary in order to reduce adverse influences of excessive deposition and/or adhesion of the calcium phosphate-based scales formed from the corrosion inhibitor and calcium components in the cooling water system on the surface of the metal members. Any polyelectrolyte can be used as long as it has effects in

preventing deposition and/or adhesion of the above-described scales. The polyelectrolyte may be acrylic acid-based polymer produced by copolymerizing monomers of (meth)acrylic acid or its salt and monomers containing a sulfonate group. The specific examples of the polyelectrolyte include a copolymer of (meth)acrylic acid or its salt and 3-hydroxy-2-allyloxy propanesulfonic acid, a copolymer of (meth)acrylic acid or its salt and isoprenesulfonic acid and/or hydroxyethyl methacrylate, etc. The polyelectrolyte may be added at an amount of 50 to 300 mg/L, preferably 10 to 100 mg/L as a solid content if necessary according to the conditions of the cooling water system to be treated.

[0027]

The primary initial treatment process for forming the initial anticorrosive film is performed for 5 to 36 hours, preferably 5 to 24 hours.

[0028]

In the present invention, after the primary initial treatment process is completed, the pH is adjusted to 7.0 to 7.5, and the initial treatment process (secondary initial treatment process) is further conducted. During the secondary initial treatment process, a calcium phosphate-based film is further formed on the initial anticorrosive film, thereby the anticorrosive film is further strengthened.

[0029]

In order to increase the pH to 7.0 to 7.5, an alkali is added. The alkali is preferably sodium carbonate or sodium bicarbonate for preventing a sudden increase in the pH. The

adjustment of the pH to 7.0 to 7.5 can be accomplished by adjusting the M alkalinity to 20 mg CaCO₃/L or higher and lower than 40 mg CaCO₃/L.

[0030]

The total performing time of the initial treatment process including the primary initial treatment process and the secondary initial treatment process is preferably 70 to 150 hours, more preferably 70 to 100 hours.

[0031]

After the initial treatment process is completed, the concentration level of the cooling water system is increased gradually to bring the cooling water system into the normal operation.

[0032]

In the present invention, a slime inhibitor, a scale inhibitor or other corrosion inhibitors may be added to the cooling water system during the initial treatment process and the following processes.

Examples and Comparative Examples

[0033]

The present invention will be described in detail with reference to Experiments, Examples and Comparative Examples.

[0034]

[Experiment 1]

Experiment was conducted regarding influence of performing time in the primary initial treatment process.

[0035]

RO water (reverse osmosis water) of which the calcium

hardness was 0 mg CaCO_3/L was fed into a 1L beaker, and then the calcium hardness was adjusted to 50 mg CaCO_3/L by adding $\text{Ca}(\text{NO}_3)_2$, the M alkalinity was adjusted to 50 mg CaCO_3/L by adding NaHCO_3 , the total phosphate concentration was adjusted to 100 mg PO_4/L by adding sodium hexametaphosphate, and the zinc concentration was adjusted to 20 mg Zn/L by adding zinc chloride. After that, the pH was adjusted to 6.0 by sulfuric acid.

[0036]

Iron sensors (each consisting of an iron rod composed of SS400 and having a diameter of 10mm and a length of 30mm) and SUS sensors (each consisting of a rod composed of stainless steel and having a diameter of 10mm and a length of 30mm) were immersed in the water in the beaker and the beaker was placed in a constant-temperature bath of 30°C as shown in Fig.2, and then the water in the beaker was stirred by a stirrer.

[0037]

The primary initial treatment process was performed for 1, 2, 3, 4, 5, 24, 48 or 72 hours. After that, the pH was adjusted to 7.0 to 7.1 by adding sodium carbonate solution. The stirring of the water in the beaker by the stirrer was continued further for 3 days, and then the initial treatment process was completed.

[0038]

In order to examine the corrosion resistance of the iron sensors (iron rods) each treated by the above initial treatment process, the water in the beaker was replaced with tap water supplied at Nogi town, and the stirring of the water in the beaker was continued for another 3 days. Then on the third day, the corrosion rate of each iron sensor was measured by a corrosion

meter (K600, manufactured by Toho Giken Ltd.).

[0039]

The results of the measurement are shown in Fig.3. Fig.3 shows that the corrosion rate was decreased remarkably by maintain the pH at 6.0 for 5 to 36 hours, specifically 5 to 24 hours during the primary initial treatment process.

[0040]

[Experiment 2]

Experiment 2 was conducted in the same manner as the case in which the pH was maintained at 6.0 for 5 hours in Experiment 1 except that the calcium hardness of the water in the beaker was adjusted to 0, 25, 40, 60, 75 or 100 mg CaCO_3/L . The results of the measurement of the corrosion rate are shown in Fig.1.

[0041]

Fig.1 shows that the corrosion rate was decreased when the calcium hardness was in the range of 25 to 75 mg CaCO_3 , especially 40 to 60 mg CaCO_3/L .

[0042]

[Example 1]

An experiment was conducted in an open recirculating cooling water system having a circulating water flow rate of 15000 m^3/hr as shown in Fig.4. The cooling water had the calcium hardness of 50 mg CaCO_3/L and the M alkalinity of 50 mg CaCO_3/L .

[0043]

Sodium hexametaphosphate and zinc sulfate were added to the cooling water system in order to adjust the total phosphate concentration to 100 mg PO_4/L and the zinc concentration to 20 mg Zn/L , and the pH was adjusted to 6.5 by sulfuric acid. The pH was

adjusted to maintain its level at 6.5 or higher and lower than 7.0 by sulfuric acid for 5 hours after a circulating pump started to operate. After that, the pH adjustment by sulfuric acid was stopped. Then after 20 hours had lapsed, the pH increased to 7.1 naturally. A carbon steel tube (STB340) was provided beside a cooling tower as a monitor heat exchanger. An evaluation was conducted by letting steam flow inside the tube and letting the circulating cooling water flow outside the tube (a shell side). The circulating cooling water flowed at a velocity of 0.1m/s at the shell-side. The heat exchange was caused by steam heating, in which Δt was 5 °C (the temperature of the cooling water was increased from 30°C at the inlet of the tube to 35°C at the outlet of the tube). The initial treatment process was conducted while maintaining the above conditions for 3 days.

[0044]

After that, a keeping process was conducted for about 1 month, in which the cooling water system was kept at conditions of the pH of 8.5 to 9.0, the calcium hardness of 150 to 250 mg CaCO_3/L and the M alkalinity of 150 to 250 mg CaCO_3/L , and added with hydroxy ethylidene diphosphate, zinc chloride, and acrylic acid/allyloxy hydroxy propanesulfonic acid copolymer (AA/HAPS) in order to adjust the total phosphate concentration to 3 to 7 mg PO_4/L , the zinc concentration to 1 to 3 mg Zn/L , and the solid content to 5 to 15 mg solid/L, respectively. After that, the carbon steel tube was detached from the monitor heat exchanger unit, and then the depth of the pitting corrosion thereon was measured. The result thereof was that the maximum depth of the pitting corrosion was 0.4mm.

[0045]

[Comparative Example 1]

The experiment was conducted in the same manner as Example 1 except that the pH was adjusted to 6.5 at the beginning of the process, but was not adjusted during the following processes. As a result, the pH increased to 7.5 in 10 minutes after the circulating pump started to operate. The pH after 3 days was 7.5. The corrosion rate was measured in the same manner as Example 1, and the maximum depth of the pitting corrosion was 0.6mm, which was 1.5 times deeper than that of Example 1.

[0046]

The maximum depth of the pitting corrosion of Example 1 was about 67% of that of Comparative Example 1, and thus the effect of preventing corrosion of Example 1 was enhanced. This indicates that according to the present invention, the duration of life of the heat exchanger can be increased.

[0047]

Although the present invention has been described in detail based on specific embodiments, the person skilled in the art will understand that various modifications are possible within the spirit and the scope of the present invention.

The present application is based on a Japanese patent application filed in the Japanese Patent Office on March 26, 2010 (Japanese Patent Application No. 2010-071677), the entire contents of which are incorporated herein by reference.

Claims

1. A method for treating a cooling water system comprising an initial treatment process for forming an initial anticorrosive film on the surface of a metal member of the cooling water system by adding a phosphate and a zinc compound to the cooling water system when the cooling water system starts to operate,

wherein said initial treatment process comprises a primary initial treatment process and a secondary initial treatment process,

the primary initial treatment process is performed for 5 to 36 hours under the conditions of a total phosphate concentration of 70 to 120 mg PO_4/L , a zinc concentration of 10 to 30 mg Zn/L , a calcium hardness of 25 to 75 mg CaCO_3/L , and a pH of 6.0 or higher and lower than 7.0, and

the secondary initial treatment process is performed under the condition of a pH of 7.0 to 7.5.

2. The Method for treating a cooling water system according to claim 1, wherein the primary initial treatment process is performed for 5 to 24 hours.

3. The Method for treating a cooling water system according to claim 1 or 2, wherein the calcium hardness is maintained at 40 to 60 mg CaCO_3/L during the primary initial treatment process.