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(54) **Boiler double buffers.**

(57) Methods of treating a steam generating system and inhibiting corrosion of metallic surfaces which comprises the step of adding to the aqueous phase of the system a non-oxygen containing alkylated diamine having at least two carbon atoms between the diamine nitrogen atoms.

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The present invention relates to methods for controlling metal loss in boiler/condensate steam systems. More particularly, the present invention relates to methods of controlling pH by feeding a single control agent to inhibit corrosion in both the liquid and steam phases of a boiler system.

Corrosion in steam generating systems, especially of iron and copper, results in damage to piping and equipment as well as the loss of high quality water and energy. The corrosion products and process chemicals if returned to the boiler can contribute to the formation of damaging boiler deposits thereby reducing the overall system reliability and increasing operating and maintenance costs.

As water temperatures rise,ferrous hydroxide is converted to magnetite (Fe_3O_4) in the absence of oxygen to form a protective film barrier. In actual boiler systems the presence of contaminants such as dissolved oxygen and carbon dioxide promote corrosion reactions.

In addition to iron corrosion in water which is augmented by the presence of oxygen, corrosion of copper by oxygen may also occur. If copper complexing agents such as ammonia are present, a protective copper oxide film cannot become permanently established. High concentrations of carbon dioxide in the condensate system, at lower pH values (less than 8), have an effect similar to ammonia in dissolving a copper oxide film.

Due to the aqueous solubility of carbon dioxide when water is heated in steam generating systems, the concentration of carbon dioxide in the water decreases and the gas enters the produced steam. Upon condensation, carbon dioxide again dissolves in the water to form carbonic acid. Since the condensate contains relatively few dissolved solids and thus little buffering capacity, the carbonic acid can drastically lower the condensate pH. In turn, when acidic condensate mixes with makeup water, the steam generator feedwater pH can also decrease.

Waters containing carbonic acid cause acidic or general corrosion of the iron and copper metallurgies found in condensate and feedwater systems. This type of corrosion is evidenced by a general wastage or by grooving of the metal surface. If untreated, corrosion can cause failure of condensate return lines, feedwater piping, and other equipment (condensate receivers, pumps, heaters, etc.) associated with steam generating and hot water heating systems.

Several methods have been devised to control acid-induced corrosion in these systems. Materials can be added that adsorb to the metal surface to form a thin barrier between the metal and the acidic solution. Examples of effective barrier forming materials that are routinely used are long chain amines, such as octadecylamine, and azoles such as tolyltriazole.

A second, more often utilized method of controlling carbonate caused corrosion is the addition of volatile amines to neutralize the carbonate and thereby increase the aqueous pH. Many different volatile amines are utilized, but some commonly used materials include cyclohexylamine, morpholine, and methoxypropylamine. On an equal weight basis, the most effective amines are those that possess high basicity and low molecular weight. The high basicity allows attainment of high pH after acid neutralization, and low molecular weight allows a greater molar concentration (and thus more neutralization). The addition of volatile amines neutralizes the acid (H^+) generated by the solution of carbon dioxide in condensate. The amines hydrolyze in water to generate the hydroxide ions required for neutralization. By regulating the neutralizing amine feedrate, the condensate pH can be elevated to within a desired range (e.g. 8.5 to 9.5). Numerous amines can be used for condensate pH neutralization and elevation. The selection of the appropriate amine is currently controlled by the basicity, stability and distribution ratio characteristics of the particular amine.

Steam generating systems are operated under several different control programs, but the general purpose of all boiler control programs is to minimize corrosion of the metal surfaces. This is accomplished by maintaining the pH within a specific window of operation, a window determined experimentally to fit the particular metallurgy, chemistry, and pressure of the system. In high pressure systems, the feedwater is very pure with little hardness and iron, and little to no organic contaminants. The boiler control methodology is designed to maintain a passive magnetite layer on the iron metallurgy and prevent adverse corrosion reactions at metal surfaces.

The solubility of magnetite is very pH dependent, with the minimum in a specific pH range. Boiler corrosion control is designed to operate in this pH window of magnetite solubility and to prevent excessive deposition while maintaining a thin magnetite layer for passivity. This control scheme is designed to maximize the efficiency of heat transfer across the boiler and condensate surfaces. Maintaining a passive magnetite is critical on both the liquid and steam side of steam generating systems. Control agents, either a single component or a mixture of additives, must be able to maintain the pH of both aqueous phases near the magnetite pH minimum. High pressure (above about 14450 kpa, (1500 psig)) steam generating equipment control agents can be categorized into two groups; inorganic and organic. Inorganic agents are typically phosphate or borate-based, while the organic systems are usually amine-based with varying physical properties.

Inorganic control agents preserve the boiler water chemistry in a non-corrosive state and are very effective at preventing problems on the water side of a steam generating system. However, they are of limited effectiveness on the steam side. Typical inorganic control agents must be used in combination with a volatile additive in order to provide pH control in the steam phase. Also, inorganic control agents often form insoluble salts with hardness and iron contaminants resulting in increased deposition. Thus, inorganic control agents are not typically employed on the steam side because of solubility and/or deposition problems.

Typical organic control agents can usually be classified as only either highly volatile or less volatile. The highly volatile agents have very short residence times in steam generators and will tend to maintain the pH of the steam phase only. The less volatile amines tend to maintain the pH of the liquid aqueous phase with limited activity in the steam phase. In addition, organic additives tend to thermally decompose and form potentially corrosive species such as ammonia and or low molecular weight organic acids. Such decomposition can be caused by high temperatures and has been a matter of concern.

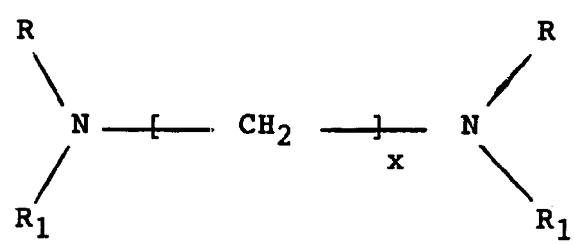
If control of both phases was needed, mixtures of materials were thought to be needed. Indeed, in the current use of organic boiler control agents, amine blends are employed to minimize these problems by providing a formulation which provides both high and low volatilities. However, such mixtures, while effective control agents, have undesirable properties such as low flash points, incompatibility with other additives, etc.

It has now been found that a specific group of amines is capable of providing, individually pH control in both the liquid and vapor phases of a steam generating system while exhibiting a resistance to degradation into ammonia. Thus, the present invention relates to methods of controlling the pH of a steam generating system in which a single amine pH control treatment agent is employed. The amine control agents of the present invention are "double buffers" which help to maintain the pH of both the liquid and steam phases within the system in a preferred range, typically 8.5 to 9.5. The control agents of the present invention also exhibit a strong buffering capacity and do not significantly break down into ammonia within a steam generating system. The control agents of the present invention maintain the pH values of both liquid and vapor (steam) phases in a steam generating system by the addition of a single "double buffer" amine.

According to the present invention there is provided a method of inhibiting corrosion of metallic surfaces in both the liquid and vapour phases of a steam generating system which comprises providing a steam pH above 8.5, a blow down pH above 8.5, a difference between steam and blow down pH not greater than 1.5 and ammonia levels in the steam and blow down not greater than 0.4 ppm by adding to the aqueous phase of a steam generating system a non-oxygen containing alkylated diamine having at least two carbon atoms between the diamine nitrogen atoms.

According to the present invention there is also provided a method of treating a steam generating system which comprises maintaining the pH of the liquid and vapour phases of a steam generating system within the range of 8.5 to 9.5 and providing ammonia levels in the liquid and vapor phases of not greater than 0.4 ppm by adding a non-oxygen containing alkylated diamine having at least two carbon atoms between the diamine nitrogen atoms.

The non-oxygen conforming alkylated diamines with at least two carbons between the diamine nitrogen atoms preferably have the general formula:



wherein the R's which may be the same or different are H or alkyl, the R_1's which may be the same or different are H or alkyl, R and R_1 are not both H and x equals 2 or more and is preferably 2 to 6.

Exemplary diamines include:
N,N,N[1],N[1]-tetramethylethylenediamine, N, N[1]-dimethylethylenediamine, and N,N,N[1],N[1]-tetramethylpropylenediamine. The control agents used in the present invention exhibit very little decomposition to ammonia in either the steam or liquid phases while maintaining both steam and liquid phase pH above a threshold level. The control agents are effective when added at relatively low concentrations.

By means of the present invention there has been discovered a specific class of amines which act as "double buffers" in the treatment of a boiler system. By "double buffer" is meant that the control agents will effectively control pH in both the liquid and steam phases. The control agents were found to provide effective pH buffering to maintain a desirable magnetite layer throughout a boiler system at relatively low treatment concentrations. The control agents maintain a desirable magnetite layer by controlling pH to the range of about 8.5 to 9.5 The buffers used in the present invention show a resistance to degradation into ammonia.

The effectiveness of representative non-oxygen containing alkylated diamines used in the present invention was evaluated in testing performed in research scale boilers. The research boilers employed in the following example are D-shaped electrically heated stainless steel assemblies with 4000 watt electrical immersion heaters that produce about 9kg/h (19.8 pounds per hour) of steam at a maximum operating pressure of about 14450 kpa (1,500 psig). Operation of the research boilers is described in US-A- 4 288 327.

The tests were run at about 10100 kpa (1,450 psig) at 50 cycles for 44 hours with no condensate return. Daily analyses were made of the steam and blowdown (liquid) products. The feedwater for the boilers was supplied by a demineralizer train and treated with the control agent alkylated diamine. Hydroquinone at a treatment rate of 0.3 ppm was added to each feedwater tank as an oxygen scavenger. Hydroquinone was selected as the oxygen scavenger due to the need for quantitative testing for ammonia. The control agent being tested was fed at a concentration of 10 ppm in the feedwater tank. The boilers were run for 44 hours to establish equilibrium between the test chemistry and the research boiler. After 44 hours samples were analyzed for ammonia and pH.

A control agent was deemed successful if it produced the following results for this test methodology:

(1) steam pH above 8.5
(2) blowdown pH above 8.5
(3) difference between steam and blowdown pH not greater than 1.5 pH units
(4) ammonia levels in the steam and blowdown not to exceed 0.4 ppm

Table 1 summarizes the results of such testing on a variety of amines and shows the unique effectiveness of the class of amines used in the present invention.

TABLE 1

Test Run Results

All concentrations in ppm

Control Agent (10 ppm in Feedwater)	pH		Ammonia		Test Results
	BD	Stm	BD	Stm	
TMEDA	9.66	9.10	<0.05	0.09	Pos
DMEDA	9.40	9.25	0.21	0.26	Pos
TMPDA	9.26	8.66	0.27	0.22	Pos
Morpholine	8.73	8.30	0.12	0.16	Neg
DMAPA	9.48	9.02	0.33	0.75	Neg
DMA	7.32	9.76	<0.3	0.3	Neg

NOTES; BD = Blowdown
Stm = Steam
TMEDA = N,N,N,N^{1}-tetramethylethylenediamine
DMEDA = N,N^{1}-dimethylethylenediamine
TMPDA = N,N,N^{1},N^{1}-tetramethylpropylenediamine
DMAPA = Dimethyleaminopropylamine
DMA = Dimethylamine

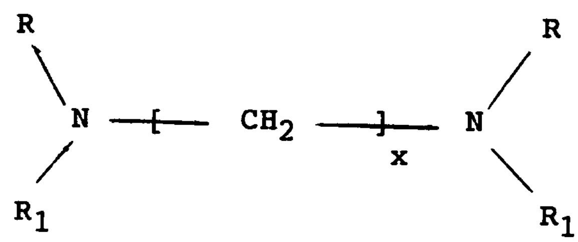
It will be seen that of the 6 different amines which were tested, only the first three (which are amines within the scope of the present invention) met the limitations of the present invention and solved the problem as discussed above in relation to the prior art. The last three, which were known in the prior art as pH control agents were all unable to control pH in both the liquid (blow down) and steam phases of a steam generating system and also unable not to degrade to undesirable levels of ammonia.

Claims

1. A method of inhibiting corrosion of metallic surfaces in both the liquid and vapour phases of a steam generating system which comprises providing a steam pH above 8.5, a blow down pH above 8.5, a difference between steam and blow down pH not greater than 1.5 and ammonia levels in the steam and blow down not greater than 0.4 ppm by adding to the aqueous phase of a steam generating system a non-oxygen containing alkylated diamine having at least two carbon atoms between the diamine nitrogen atoms.

2. A method of treating a steam generating system which comprises maintaining the pH of the liquid and vapour phases of a steam generating system within the range of 8.5 to 9.5 and providing ammonia levels in the liquid and vapor phases of not greater than 0.4 ppm by adding a non-oxygen containing alkylated diamine having at least two carbon atoms between the diamine nitrogen atoms.

3. A method according to claim 1 or 2, wherein the non-oxygen containing alkylated diamine has the general formula



wherein the R's which may be the same or different are H or alkyl, the R_1's which may be the same or different are H or alkyl, R and R_1 are not both H, and x is two or more.

4. A method according to claim 3, wherein x is two to six.

5. A method according to claim 4, wherein the non-oxygen containing alkylated diamine is selected from N,N,N^1,N^1-tetramethylethylene diamine, N,N^1-dimethylethylenediamine, and N,N,N^1,N^1-tetramethylpropylenediamine.