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SULPHITE-ERYTHORBIC ACID CORROSION INHIBITORS

The present invention relates to a method of inhibiting corrosion and scale in boiler waters.

There are two major parameters involved in inhibiting corrosion in preboiler and boiler systems. Corrosion is minimized by not only oxygen removal but, also, by the formation of protective films. Of the two major oxygen scavengers, sulfite ion is not only the most effective reducing agent, but also it is much more cost effective. It has serious drawbacks, however, the major one is its contribution to dissolved solids content (a critical parameter) in boilers. In addition, it does not promote protective films by reducing ferric and cupric ions.

Hydrazine, the other major oxygen scavenger, is a less effective reducing agent and costs much more. Therefore, it must have additional advantages. These are that it does not add solids because its decomposition and reaction products are volatile, but it also can interact with soluble ferric, cupric salts and oxides to produce lower valence state oxides which form protective films inhibiting further corrosion. This is the most important parameter for hydrazine since protective films can be formed in the presence of low levels (<10 ppb) oxygen (hydrazine is known as a passive film former).

It is also known that erythorbic acid and, also, ascorbic acid passivate metal in scale boiler studies even under conditions in which oxygen is know to still be present. In fact, erythorbic acid is much more effective in this role than either hydrazine or sulfite. It is also known that it reacts better with oxygen than hydrazine but it is less effective than sulfite.

There are several facts about ascorbic/erythorbic acid that indicate its potential role as a passivating agent. The literature reports its ability to reduce cupric to cuprous and ferric to ferrous ions. Both of these reactions are key in this role. Passivation

tests in a laboratory scale boiler show that erythorbic acid is better than hydrazine or sulfite in passivating ability.

Sulfite gives better results than hydrazine in oxygen scavenging because of its oxygen control at 41 bar gauge, ~254°C (600 psig, ~490°F). Sulfite does not significantly decompose in the boiler whereas hydrazine does. Hydrazine's reported decomposition temperature is 204°C (400°F). In addition, this material is volatile. Therefore, sulfite, which is non-volatile, maintains a reducing atmosphere in the boiler and keeps oxygen concentration at a minimum.

Many industrial plants presently use a combination of sodium sulfite and hydrazine to inhibit corrosion in the preboiler and boiler systems. This application technology is based on the use of sulfite as an oxygen scavenger and hydrazine as a passive film enhancer.

Hydrazine is a toxic material and may present a health problem when it is handled by non-chemically trained operators. For this reason, its use as a commercial chemical is becoming limited.

THE INVENTION

A method for inhibiting corrosion and scale in boiler waters which contain dissovled oxygen which comprises maintaining the said waters at a pH of at least 7, and maintaining in solution in said waters at least 5 ppm of $SO_3^{=}$ ion and at least 2 moles of an acid which may be either erythorbic or ascorbic acid per mole of dissolved oxygen.

The sulfite ion is most conveniently furnished by utilizing the well known oxygen scavenger, sodium sulfite. While other water-soluble sulfites may be used, the sodium salt is preferred. The dosage level

of sulfite ion, $SO_3^=$, that should be maintained in the boiler is at least 5 ppm with amounts ranging between 10-50 ppm being preferred, with 20-40 ppm being most preferred.

The acids used in the invention are either erythorbic acid or ascorbic acid. The most preferred is erythorbic acid. It is used at a dosage level of at least 2 moles per mole of dissolved oxygen present in the boiler waters. Amounts in excess of 2 moles may be used, but no particular advantage is gained.

An interesting fact which has previously been discovered is that both erythorbic and ascorbic acid to be effective must be utilized in boiler waters having pH's greater than 7 and, preferably, greater than 8.5, and most preferably pH's greater than 9.0.

To evaluate the invention and to show prior art comparisons, the following test method was used.

Test Method

The ability of several oxygen scavengers to passivate heat transfer surfaces was investigated in experimental research boilers. The test covered a 48 hour period and test conditions were 41 bar (600 psi), 10 cycles of concentration and 1.25 $GJ/m^2/hr$ (110,000 $BTU/ft^2/hr.$). The feedwater contained 4 ppm Ca (as $CaCO_3$), 2ppm Mg (as $CaCO_3$), and 1 ppm silica (as SiO_2). In addition, feedwaters contained various amine compounds such as morpholine, cyclohexylamine, and diethyl amino ethanol at concentrations of about 50 ppm each. These amine compounds normally are present in boiler feedwaters, so as to provide corrosion protection for the overhead condensate system within the boiler unit. Their presence or absence is not anticipated to effect positively or negatively the oxygen scavenger/metal passivating activites of the compounds of this invention. The feedwater was passed through a deaerator prior to introduction into the experimental boiler system. Final oxygen levels before treatment with the compounds of this invention were less than 50 ppb (parts per billion). Sufficient NTA[1] was in the feedwater to provide a 5 ppm residual in the boiler.

Three oxygen scavengers: hydrazine, sulfite, and erythorbic acid, and combinations thereof, were examined

during these tests. Hydrazine was fed at 2ppm, erythorbic acid at 2ppm active equivalents (i.e., 2 moles EA/1 mole hydrazine/1 mole O_2), and sulfite sufficient to provide 30 ppm $SO_3^=$ ion in solution in the boiler water. A comparison of the firerods from these tests show that erythorbic acid produces passivated surface superior to that obtained with either sulfite or hydrazine. A dark, thin, magnetite layer resulted from treatment with erythorbic acid. On the other hand, both sulfite and hydrazine produced a magnetite layer that had various degrees of discoloration due to the presence of reddish iron oxides that had not been completely converted to Fe_3O_4.

Various combinations of the above mentioned oxygen scavengers were evaluated in the scale boilers under conditions previously described. As can be seen from the Table, the combination of erythorbic acid plus sulfite is an excellent corrosion inhibition system. This test ranking surpasses all other tests conducted in the boiler for passivation potential This film was uniform, black, very thin, and difficult to scrape off.

The combination of hydrazine and sulfite was also tested and rated against either the single components mentioned above or combinations thereof. Hydrazine and sulfite combination formulations, tested in the same manner, gave results which rated substantially below the combination of erythorbic acid and sulfite and even rated measurably below erythorbic acid itself. The data is presented in the following Table.

[1]Nitrilotriacetic acid, sodium salt

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TABLE

Conditions of Test	Rating System
All feedwaters contained 4 ppm Ca (as $CaCO_3$), 2 ppm Mg (as $CaCO_3$), and 1 ppm Silica - Chelate treated to provide 5 ppm residual NTA in the boiler water tested at 41 bar, 1.25 $GJ/m^2/hr$ (600 psig, 110,000 $BTU/ft^2/hr$) and 10 concentrations. All feedwaters also contained 50 ppm each of morphine, cyclohexylamine, and diethylaminoethanol.	4 poor 4-6 acceptable 6-7 good 7-8 very good 8-9 superior 9-10 excellent

Test No.		Rating
1	$SO_3^{=}$ ion in solution at 20-40 ppm; EA at equivalent dosage to 2 ppm hydrazine where EA requires 2 moles/1 Mole O_2 and hydrazine required 1 Mole/1 Mole O_2.	10
2	Same as above but no $SO_3^{=}$.	9
3	$SO_3^{=}$ ion in solution 20-40 ppm.	7.5-8.0
4	Hydrazine at 2ppm.	7
5	Hydrazine at 2ppm; $SO_3^{=}$ ion in solution at 20-40 ppm.	8.5
6	No oxygen scavenger	0

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CLAIMS

1. A method for inhibiting corrosion and scale in boiler waters which contain dissolved oxygen which comprises maintaining the said waters at a pH of at least 7, and maintaining in solution in said waters at least 5ppm of $SO_3^{=}$ ion and at least 2 moles of an acid which may be either erythorbic or ascorbic acid per mole of dissolved oxygen.

2. The method of claim 1 wherein the level of $SO_3^{=}$ ion in solution is maintained between 20-40 ppm.

3. The method of claim 2 wherein the acid is erythorbic acid.

4. The method of claim 2 where the acid is ascorbic acid.

5. An improved method for inhibiting corrosion and scale in boiler waters, substantially as hereinbefore described.

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