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PROTECTIVE FILM FORMATION IN HIGH PRESSURE STEAM GENERATORS

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The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to the operation of steam generators, more particularly at high pressures and to the use of a new and improved alkaline-type corrosion inhibitor for protection of the steel heating surface.

It is general practice to operate steam boilers with feed water which has been alkalized by the addition thereto of small amounts of sodium hydroxide.

Due to a constantly rising demand for power, steam boilers have been operated at increasingly higher pressures over the period of the past several decades. Boiler operation has been conducted at pressures in the range of 1200 to 1400 p.s.i. and higher.

Operation of steam boilers at higher pressures has been recognized to have introduced a new type of tube corrosion. This new type corrosion derives from the occurrence in boiler tubes of locally developed strong solutions of caustic soda which attack the steel and deeply pit the tube walls at irregularly occurring areas. Potassium hydroxide will behave similarly to sodium hydroxide as the alkalizer for the boiler water.

Local strong solutions of caustic soda are developed in the tubes of steam boilers operated at the higher pressures at high rates of steam generation. Under conditions of inadequate circulation or excessive local heat throughput this condition is aggravated by the development of steam blanketing. Normally, in the operation of the boiler, small steam bubbles are formed at the tube wall which easily leave the wall to allow the steam to course down the tube and sufficient water moves to the tube wall to keep it at a relatively low temperature. Occasionally a large steam bubble is formed which clings to the wall. Steam is a thermal insulator and the bubble-covered area of the wall is raised to a temperature considerably above normal by the high input of heat to the tube. When, subsequently, boiler water of normal alkalinity is splashed to the overheated wall area, evaporation takes place with development of a strong solution of caustic soda.

Attack on the steel by the locally developed strong solution of caustic soda results in corrosion of the steel tube by reaction between water of the solution and iron of the steel in accordance with the equation

$$3Fe+4H_2O\rightarrow Fe_3O_4+4H_2 \qquad (1)$$

A layer of the solid product of the corrosion reaction, which is the magnetic iron oxide, Fe_3O_4, is deposited on the steel of the area. By continuance of the reaction, a relatively thick layer of the corrosion product is formed over the affected area of the tube wall. During the formation of this relatively thick layer of the corrosion product, the solution of caustic soda penetrates the corrosion layer and lodges beneath it. The rate of heat input to the tube being high, concentrations of the trapped solution in caustic soda takes place as a result of the combined effects of evaporation of water and continuance of the reaction in which water is consumed. Caustic soda is a promoter of the corrosion

reaction, and by development of the solution of greater caustic soda concentration beneath the corrosion layer, acceleration of the reaction takes place with consumption of steel in the pocket holding the solution. The direction of the progression of the corrosion reaction is now into the tube wall and by repeated concentrating of the pocketed solution in caustic soda and consequent acceleration of the corrosion reaction a pit is developed in the wall of the steel tube. Frequently, the pitting reaction will continue until the tube wall is pierced.

Pitting corrosion in the operation of steam boilers at the higher pressures has been a problem for several decades and has remained so to the present time. This type of corrosion is accountable for a high annular rate of tube replacement.

It is an object of the present invention to provide a new and improved alkaline-type corrosion inhibitor for use in the boiler water of steam generators which are operated at high pressures. It is a further object to provide a method of operating steam generators at high pressures in which pitting corrosion of steel is avoided and the benefits of alkalinity in the boiler water retained.

We have found by our invention that steam generators can be operated at high pressures with freedom from the occurrence of pitting corrosion of steel tubes when the boiler water is alkalized with lithium hydroxide to a pH in the range of about 9 to 13 and preferably in the range of 10 to 11.

The practice of the method of the invention using boiler water which has been alkalized with lithium hydroxide for the generation of steam at high pressures does not require any departure from general procedures observed in operating high pressure steam generators. The feed water may be treated with a solution of the lithium hydroxide in the customary way for the addition of sodium hydroxide to feed water. For a pH in the range 9 to 13 in the feed water, the concentration of lithium hydroxide in the water should be from 0.24 to 2400 parts per million (p.p.m.).

Aqueous solutions of lithium hydroxide behave differently than do aqueous solutions of sodium or potassium hydroxide in respect to reaction with steel at high temperatures.

At low concentrations, corresponding to normal alkalinity in boiler water in the usual steam generation process, water of an aqueous solution of LiOH, NaOH or KOH will react in accordance with the equation:

$$3Fe+4H_2O\rightarrow Fe_3O_4+4H_2 \qquad (1)$$

to deposit a protective film of the magnetic iron oxide, Fe_3O_4, on the steel heating surface of the boiler.

When, by evaporation of water, concentration of the alkali hydroxide takes place in the solutions in the presence of steel at high temperatures, the behavior of the LiOH solution is distinctly different from that of the NaOH and KOH solutions.

The concentrated solutions of NaOH and KOH will continue to react with the heated steel in accordance with Equation 1 to generate the corrosion product, Fe_3O_4. Since Reaction 1 consumes water, a further concentration of the solutions in NaOH and KOH will take place at the site of the reaction.

On evaporation of water from the lithium hydroxide solution with concentration to substantially less than 1%, a second and different reaction occurs for LiOH in accordance with the following equation:

$$5Fe_3O_4+3LiOH+H_2O\rightarrow 3LiFe_5O_8+5/2H_2 \qquad (2)$$

which deposits an adherent tight protective film of the lithium enriched spinel, $LiFe_5O_8$, on the steel.

Should the circumstance happen that a concentration of LiOH in the aqueous solution in the neighborhood

of 1% is effected at the heated steel surface the following reversible reaction will take place:

$$LiFe_5O_8+4LiOH \leftrightharpoons 5LiFeO_2+2H_2O \quad (3)$$

This will relieve the concentrated condition of the solution at the site by withdrawing LiOH in forming $LiFeO_2$ and supplying water.

This reversible reaction limits the concentration of LiOH achievable at the corrosion site to the neighborhood of 1%, the equilibrium concentration for this reaction, for as soon as this concentration is exceeded the LiOH will be used up and water will be generated by the reaction going to the right. The existence of the $LiFeO_2$ is transitory however, because as this reaction proceeds to the right, the water generated in the reaction reduces the LiOH concentration to below the equilibrium value and the reaction then proceeds to the left. This equilibrium concentration of LiOH in the solution at the corrosion site is so low as not to allow the development of pitting at the site.

The method of the invention may be practiced with benefit of the foregoing advantages in the operation of steam generators at high pressures which may range from a low of around 350 p.s.i. to a median of about 1400 to 1500 p.s.i. and higher. The only limitation on securing the advantages which may be derived from the use of lithium hydroxide in alkalizing the boiler water is that of structural design of the steam generator to withstand desired high operating pressures.

Since various changes and modifications may be made in the practice of the invention without departing from the spirit or scope thereof, it is not intended to be limited except as may be required by the appended claims.

What is claimed is:

1. In the operation of a steam generator at high pressures of at least 350 p.s.i. in which the steam is produced by contacting the water with a heated steel surface, the improvement which comprises operating said steam generator at said high pressures with boiler feed water which is alkalized with lithium hydroxide in solution therein to a pH in the range of 9 to 13.

2. In the operation of a steam generator at high pressure of at least 350 p.s.i. which the steam is produced by contacting the water with heated steel surface, the improvement which comprises operating said steam generator at said high pressures with boiler feed water which is alkalized with lithium hydroxide in solution therein to a pH of about 10 to 11.

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