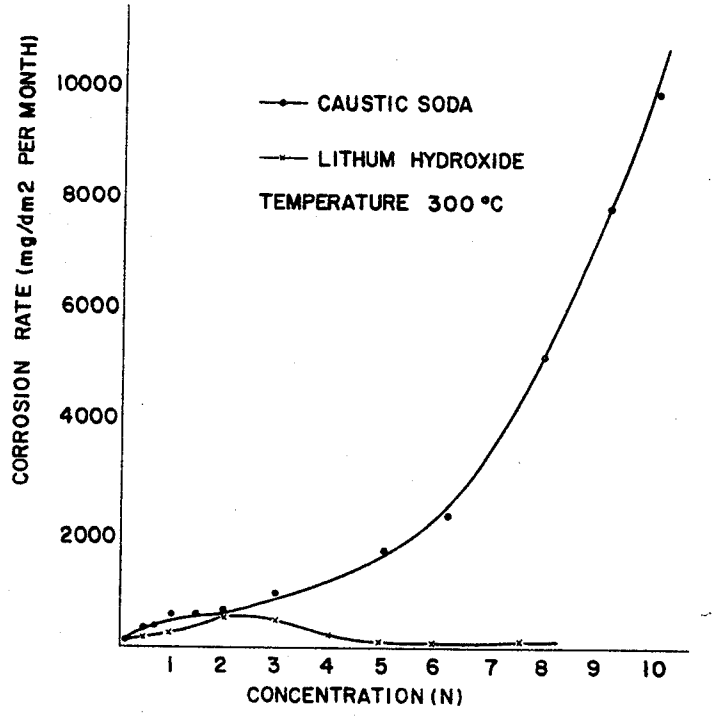
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METHOD FOR THE PROTECTION OF INTERNAL SURFACES OF THE TUBES FOR HIGH-TEMPERATURE, HIGH-PRESSURE BOILERS FROM CORROSION

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METHOD FOR THE PROTECTION OF INTERNAL SURFACES OF THE TUBES FOR HIGH-TEMPERATURE, HIGH-PRESSURE BOILERS FROM CORROSION

Osamu Asai, Hitachi-shi, Japan, assignor to Kabushiki Kaisha Hitachi Seisakusho, Tokyo-to, Japan, a joint-stock company of Japan

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3 Claims. (Cl. 148—6.14)

ABSTRACT OF THE DISCLOSURE

A method for the protection of the internal surfaces of tubes in high-temperature, high-pressure boilers from corrosion by passing through these tubes a lithium hydroxide solution after pickling. The LiOH wash promotes formation of a heavy iron oxide film which substantially decreases the corrosion rate of the tubes.

This application is a continuation-in-part of my application Ser. No. 307,193, filed Sept. 6, 1963, now abandoned.

In an evaporative tube of a boiler being used at a new modernized thermal power plant, it sometimes happens that the boiler water is concentrated in the portion adjacent to the tube surface thereby becoming a highly concentrated alkaline solution which often causes severe corrosion on the tube surface because of the prevailing high temperature and high pressure. As a method of preventing such corrosion as described above, mill-scale, red rust and other corrosion products formed on the internal surface of a boiler have heretofore been removed by a washing treatment commonly known as so-called pickling at the time of inspection prior to commencement of the operation after the erection of the boiler as well as at the time of annual periodic inspections. Such a treatment is resorted to because the existence of said adherent substances on the internal surface of the boiler is the principal cause of the above-mentioned corrosion. Since the metallic surface is very susceptible to corrosion after such adherent matters have been removed by pickling, some additional anti-corrosion treatment must be carried out. The simplest method for this latter treatment is to pass an alkaline solution of sodium phosphate, caustic soda, or their mixture with sodium carbonate through the metal tubes so as to neutralize the remaining acid liquid and form an anti-corrosion film on the surface of the metal tubes.

By the use of said alkaline solution, iron hydroxide will be formed on the internal walls of the tubes in a steel boiler according to the following formula

$$Fe^{++}+2OH^{-}\rightarrow Fe(OH)_2 \quad \text{or} \quad Fe^{+++}+3OH^{-}\rightarrow Fe(OH)_3 \qquad (1)$$

Next, since the boiler is to be heated to approximately 300° C., the iron hydroxide will decompose in accordance with the following chemical reaction

$$3Fe(OH)_2\rightarrow Fe_3O_4+2H_2O+H_2 \qquad (2)$$

or

$$3Fe(OH)_3+\tfrac{1}{2}H_2\rightarrow Fe_3O_4+5H_2O \qquad (3)$$

whereby an anti-corrosion film of Fe_3O_4 forms on the interior surface of the iron tube.

However, although this kind of liquid can neutralize the acid liquid, it has been impossible to form a metallic oxidized film which is truly protective against corrosion on the surface of the metal tube.

As a result of various studies, the inventor has come to the conclusion that, in the formation of a film by use of said alkaline solution, the above-mentioned inability of forming a truly protective film is probably due to the chemical weakness of the film against the alkaline solution, and to the fact that the formed film has many defects such as the formation of extremely small pin-holes, cracks and crystal defects. As a result of studies based on said conclusion, this invention has been developed.

An essential object of this invention is to provide a method of protecting the boiler tubes from corrosion without the accompaniment of the above-mentioned various difficulties.

Said object and other objects of this invention have been attained by passing a lithium hydroxide solution through the metal tubes at least once during the course of neutralization of acid liquid and the formation of anti-corrosion film on the interior surface of tubes.

The lithium hydroxide solution to be used as a treatment solution in this invention is contained in conventional alkaline solutions which have been in use heretofore. However, no study whatsoever has been made of this lithium hydroxide solution, and consequently the remarkable effect derived from said substance has not yet been generally known. The cause of this remarkable effect, i.e., the excellent anti-corrosion effect, has not yet been clarified sufficiently, but it is considered that, first of all, the Fe_3O_4 film obtained by the treatment with lithium hydroxide solution is free from said defects, differing from the Fe_3O_4 film formed by caustic soda solution. In any case, the fact that the film formed by the use of lithium hydroxide has an excellent anti-corrosion property has been confirmed by a large number of experimental data.

The following is an example of such data:

Conditions:	Corrosion rate (mg./dm.^{2} month)
1. In the case of subjecting to corrosion with 1 N NaOH at 300° C. (after 200 hrs.)	500
2. In the case of subjecting to corrosion with 1 N LiOH at 300° C. (after 200 hrs.)	200
3. In the case of subjecting to corrosion with 1 N NaOH at 300° C. after treatment with 1 N LiOH at 300° C. for 200 hrs. (after 200 hrs.)	200
4. In the case of subjecting to corrosion with 5 N NaOH at 300° C. after treatment with 1 N LiOH at 300° C. for 200 hrs. (after 200 hrs.)	200
5. In the case of subjecting to corrosion with 1 N LiOH at 300° C. after treatment with 1 N NaOH at 300° C. for 200 hrs. (after 200 hrs.)	400

It is clear from the above table that in the case of treatment with only NaOH solution the corosion rate is very large, whereas in the case of treatment with LiOH solution, as shown in the case 2, the corrosion rate becomes less than half of that of the case 1.

An even more noteworthy fact is that, as will be clear from the columns 2, and 4, in the case of pre-treatment with LiOH solution, the succeeding treatment with NaOH solution brings about the same result in the corrosion rate as in the case of treatment with LiOH alone. Furthermore, the corrosion rate in the case of treating first with an NaOH solution and then with a LiOH solution is almost the same as when only NaOH issued in the treatment.

The essential point of this invention, therefore, is to treat first with LiOH solution. If it is uneconomical to carry out the treatment with LiOH alone, the treatment can be carried out first with LiOH solution by the treatment with NaOH, thus the film of Fe_3O_4 formed on the

surface of a steel tube is rendered thicker, whereby the corrosion rate decreases.

The advantages and other features of this invention will become more apparent by the following description of the relationship between corrosion rates and the concentration of alkali solution, taken in connection with the accompanying drawing, in which a graph with curves indicating the said relationship is shown.

As the drawing clearly shows, when the concentration of the alkaline solution is low, the difference in the corrosion rate between the LiOH and NaOH is not particularly large. However, the drawing also clearly shows that an LiOH solution of as low as 0.1 normality has a better anticorrosive effect than a corresponding NaOH solution. When the concentration is near 2 N, the difference between the two solutions is the slightest, but beyond that concentration, the difference in the corrosion rate grows rapidly, the effect of LiOH becoming substantially steady whereas the corrosion rate steeply increases when using NaOH.

Thus, the method of preventing corrosion according to this invention has a remarkably excellent anti-corrosion effect in comparison with conventional methods and can be used most advantageously, particularly when the water of a boiler, as in the case of a high-temperature, high-pressure boiler, has a tendency to become an alkaline solution of high concentration.

I claim as my invention:

1. A method of protecting the internal wall of evaporative tubes used in a high-temperature, high-pressure boilers which consists essentially of passing an aqueous solution of lithium hydroxide at least once through said tubes in the course of neutralization of acid liquids and formation of an anti-corrosion film on the internal surface of said tubes, said solution containing a sufficient number of lithium ions to produce an Fe_3O_4 protective film which is free from defects.

2. The method as defined in claim **1**, wherein the passing of said lithium hydroxide solution is followed by passing a substantially 1 to 2 normal sodium hydroxide solution.

3. The method as defined in claim **1**, wherein said solution of lithium hydroxide is in the range of from 0.1 to 8 normal.

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RALPH S. KENDALL, *Primary Examiner.*