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SUBJECT: Chemical Cleaning and Storage of the HRT Steam and Closed Cooling Water Systems

TO: Distribution

FROM: H. A. McLain

Summary

A 10% phosphoric acid solution containing 0.2% "Rodine 45" inhibitor is recommended to be used for the chemical cleaning of the HRT steam and closed cooling water systems. Wet storage is recommended for both of these systems. The steam system is to be stored with steam condensate containing 100 ppm hydrazine, and closed cooling water system is to be stored with steam condensate containing 1000 ppm potassium chromate.

Chemical Cleaning Materials

Chemical cleaning is used widely for the removal of corrosion products and other water-insoluble deposits from the surfaces of power plant and cooling water systems.(1)(2) Inhibited hydrochloric acid is the material most widely used for chemical cleaning because of its relatively low cost and the availability of inhibitors. This material cannot be used for the HRT, however, because of the possibility of promoting stress corrosion cracking in the stainless steels.

Three other acids were considered and tested for the chemical cleaning of the HRT systems; sulfuric acid, citric acid, and phosphoric acid. "Rodine 45" was used as the inhibitor for the citric and phosphoric acid solutions, and the sulfuric acid was tested in the form of a commercial inhibited acid preparation called "Duclean". The laboratory tests showed that phosphoric acid inhibited with "Rodine 45" is most satisfactory for the cleaning of the HRT systems. This solution will remove the mill scale, rust, and other corrosion products, but is relatively harmless to the system, removing only about a mil (per cleaning treatment) of carbon steel and negligible amounts of the other materials in the steam and water systems.(3) This is in agreement to what is reported in the literature(1,2,4). This assumes that there is no aluminum or zinc in the systems which the phosphoric acid will readily attack. Removal

of zinc is not considered serious since the galvanizing inside the HRT closed cooling water system probably has already corroded away.

Another advantage of using phosphoric acid in preference to the other acids is that the metal surfaces after cleaning are passivated and objectionable rusting immediately after treatment is prevented.[1,2] This is particularly important when the surfaces are in a moist condition before the acid is neutralized.

Tests on the cleaning of a small corroded heat exchanger showed that a 10% solution is a desirable compromise of the cleaning properties and the attack on the metal surfaces.[5]

Chemical Cleaning Procedure

The procedure for cleaning the HRT steam and closed water systems is based on information reported in the literature[1][2][4], laboratory tests,[3] and tests on a small corroded test heat exchanger[5]. This information showed that a phosphoric acid cleaning followed by dilute phosphoric acid and trisodium phosphate solution rinses would be satisfactory. The dilute acid rinse is for removing the dissolved iron in the film which has adhered to the metallic surfaces during the draining of the phosphoric acid cleaning solution. Water would precipitate the iron on the surfaces. The trisodium phosphate solution rinse is for the purpose of neutralizing the residual acid remaining in these HRT systems.

An outline of the recommended cleaning procedure is as follows:

1. Phosphoric acid cleaning

   Circulate 10% acid solution 8 hours at 65°C.

   Sample and analyze (100 ml samples) every hour to maintain 10% concentration by the addition of acid as required.

   Drain.

2. Dilute acid rinse.

Circulate 0.1% acid solution for a few minutes at 65°C.

Sample (100 ml sample).

Drain.

3. Water rinse.

Circulate warm potable water for a few minutes.

Sample (100 ml sample).

Drain.

4. Alkaline rinse.

Circulate 0.5% trisodium phosphate solution 12 hours at 65°C.

Sample and analyze every 2 hours (100 ml samples) in order to maintain the solution's pH above 8.

Drain.

5. Water rinse.

Circulate warm steam condensate for a few minutes at 65°C.

Sample (100 ml sample).

Drain.

The composition of the chemical solutions required to carry out the above procedure are as follows:

1. 10% phosphoric acid solution.

10.0% H_3PO_4

0.2% "Rodine 45"

For one liter of this solution, use

71.6 ml concentrated (85% H_3PO_4) phosphoric acid

2.0 ml "Rodine 45"

926 ml potable water

2. 0.1% phosphoric acid solution.

0.1% H_3PO_4

0.2% "Rodine 45"

For one liter of this solution, use

0.7 ml concentrated (85% H_3PO_4) phosphoric acid

2.0 ml "Rodine 45"

997 ml potable water

3. Trisodium phosphate solution

0.5% Na_3PO_4

For one liter of this solution, use

5 gms trisodium phosphate

1 liter potable water

As indicated above potable water may be used for these solutions and the initial water rinse. For the final water rinse, however, steam condensate is recommended in order to keep the residual chloride concentration in these systems down to a minimum. All chemicals used in these solutions must first be checked for excessive amounts of chlorides.

Provisions must be made for the venting of gases from the high points of the HRT systems during cleaning. This is made necessary by the fact that hydrogen will be generated during the cleaning process[1,2] and will present a hazard unless properly removed. Also, provisions should be made for draining of the solutions from the low points of the systems if possible in order to remove mill scale or any other material that may accumulate at these points during the cleaning process.

Finally, the effectiveness of the cleaning should be visually inspected wherever it is readily possible.

Storage

Wet storage is recommended for the HRT steam and closed cooling water systems after their cleaning. The TVA has found that wet storage is best for their standby boilers.(6)

In view of the TVA's experience(6), a solution of 100 ppm of hydrazine in steam condensate is recommended for the storage of the HRT steam system. The TVA has found that the hydrazine loss is about 2 to 3 ppm per month after the iron oxides have been reduced. It is recommended that the storage solution be checked for hydrazine about once a day during the initial period of storage since the hydrazine losses will be comparatively large at first because of the reduction of the iron oxides. Once these oxides have been reduced, however, the loss of hydrazine should be small and the sampling will be required only once a week or perhaps once a month. The storage solution should be circulated occasionally, particularly during the fore part of the storage period, in order to prevent pockets in the solution which are depleted in hydrazine. If this should occur, corrosion would be enchanced instead of prevented.

The closed cooling water system should be stored with steam condensate containing 1000 ppm potassium chromate.(1,2) This solution should prevent corrosion in this system, and since it will also be the solution used in this system during the operation of the reactor, the system will be ready to operate with the starting of the pumps. Sampling of this storage solution during the storage period need be made only once a week or perhaps once a month.

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References

1. W. H. and L. D. Betz, Betz Handbook of Industrial Water Conditioning, 4th Ed., W. H. and L. D. Betz, Philadelphia, (1953).

2. S. T. Powell, Water Conditioning for Industry, McGraw-Hill Book Co., New York, (1954).

3. P. D. Neumann, Personal Communication.

4. T. E. Purcell and W. F. Whirl, "Phosphoric Acid Cleaning for High Pressure Boilers and Auxiliary Equipment," Power Engineering, 54, 8:72, (1950).

5. Tests were performed by J. W. Hill, Jr.

6. C. H. Waugaman, Personal Communication.

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