## **Corrosion control in boiler turbine systems**

NEOGI, P.S \*, MEHTA, R J \*

#### Introduction

Corrosion in the boiler water systems is normally attributed to ingress of Carbon-di-oxide or Oxygen Performance of boiler systems and turbines is also hampered by deposits of salts, which result in reduction of heat transfer, high metal temperatures and increased maintenance cost resulting from frequent cleaning.

The conventionally method of feed water treatment after the normal softening or Demineralisation process include addition of Phosphates, Hydrazene/ Sulphite, and Ammonia/Sodium Hydroxide etc. This treatment leads to the formation of a Magnetite layer on the metal surfaces which in principle prevents the metal surface from coming in contact with corrosion products and gases. This method has however its inherent drawbacks which are overcome by multi component polyamine treatment as discussed in the text.

This new technology of multicomponent polyamine treatment provides a foolproof protection to the complete boiler—turbine—condensate systems against corrosion attacks both inherent or accidental It basically forms a protective polyamine film on the metal surface, thus preventing attack of corrosive product and deposits.

#### Drawbacks of conventional Phosphate based treatment

The conventional treatment which is based on a combination of Phosphates, reducing agents like Hydrazene and neutralizing agents like Ammonia or Sodium Hydroxide from a hard, brittle Magnetite layer on the virgin metal surface while also scavenging Oxygen and neutralizing Carbon-di-oxide to some extent. However Oxygen corrosion "in after-boiler lines are not controlled. The basic drawback in this treatment is the brittle nature of the Magnetite layer which tends to crack under frequent thermal shocks and vibrations inherent in the boiler system. These cracks thus provide an access to the virgin metal surface for the corrosion gases and hence corrosion starts taking place beneath the layer till the time the crack is healed again. Furthermore Hydrazene does not prevent corrosion in condensate lines in case of ingress of Oxygen somewhere in the system. Hydrazene also provides practically no protection at temperatures above 280 Deg C as it then breaks down to Ammonia.

This treatment also does not cater to the requirement of protection on the condensing side of the turbines which are often exposed to Silica deposits. This becomes crucial because such deposits adversely affect the performance of the turbine apart from being expensive in monetary terms due to the cleaning involved.

Another fallacy of the Phosphate based treatment lies in the fact that after taking extensive care to purify the feed water as much as possible, salt contamination is introduced by way of Phosphates and Sodium Hydroxide which lead to higher boiler blowdowns to control the TDS levels.

Furthermore, Phosphates are dosed in the high pressure zones in the boilers and thus pose maintenance problems in high pressure boilers which need very high pressure dosing pumps.

In short it can be stated that the Phosphate based treatment requires very stringent feed water quality requirements as any deviation would render the treat-

\*M/s. Elof Hansson (India) Pvt. Ltd. VKP Hiam, 72 Cathedral Road Madras-600 86

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ment ineffective leading to costly failures by way of corrosion or deposits.

While the polyamine treatment has been in use abroad for a number of years now, this modern treatment based on multicomponent volatile polyamines has been introduced in India in 1988. This treatment compensates for the basic drawbacks of Phosphate treatment while providing a comprehensive protection to all moist-metal surfaces in addition to substantial energy conservation and ease of operation.

#### The Principle of Multi-Component Polyamine Treatment

Amine treatments have been tried ever since the 1950's. The first efforts were based on aliphatic primary amines. While these amines did form an adhesive protective film on moist metal surfaces, this film was somewhat unstable in nature and also did not have the desired  $CO_2$  neutralizing effect. They also required a simultaneous dosing of a dispersants. Though good protection was observed in new systems, the effect was not satisfactory in old systems which already had a certain amount of corrosion.

Further efforts towards overcoming the above problems were made in the 1960's, by using Aliphatic polyamines. The polyamines did provide a more stable film on moist metal surfaces, but still did not provide a protection in large syslems having long condensate lines as the distribution ratios were not adequate.

Volatile amines like Morpholine, Cyclo-hexalamine etc, have also been used for neutralisation of  $Co_2$  in the long condensate lines However, use of neutralizing volatile amine does not provide any protection against corrosion deposits as also against Oxygen present in the feed water.

It has since been discovered that a treatment with a multicomponent polyamine formulation which draws on the characteristics of various polyamines is extremely effective in providing a satisfactory protection against the hazards that one would normally encounter in boiler-turbine operations. Furthermore, formutations, have been patented which also provide protection against accidental ingress of corrosion products. It is to be emphasised here that the conventional phosphate based treatment does not provide any system protection against such accidents.

The successful multi-component polyamine formulations have basically the following main ingredients :

- \* Film forming polyamine
- Neutralizing polyamines
- \* Dispersing polyamines

The combination of the above provides practically a fool-proof system protection against most operational eventualities.

The basic protection to the metal surface is provided by the film forming polyamines. These form a very supple, mono-molecular (8-10 Ang thick), stable film on all divalent metal surfaces exposed to moisture. The film is a result of a strong covalent bond between the base metal and the bipolar polyamine molecules in the presence of moisture. As corrosion attack only takes place under moist conditions, the metal surface is fully protected. The suppleness of the film also eliminates any effect of thermal shocks.

The interstitial space between the molecules forming the film is of the order of 1-5 Ang; thus the film provides an inpenetrable barrier to both Oxygen and Carbon-di-Oxide molecules, whose cross-sectional areas are several times larger.

The smooth film also prevents any deposits of either Silica or Salts on the moist-metal surfaces. This is extremely important from the point of view of turbine operations as any Silica deposits are avoided on the condensing side. The film formation on the condensate lines is assured by a suitable comibation of filming polyamines having varying distribution ratios.

The neutralizing polyamines provide an added protection to ingress of  $CO_2$  anywhere in the boiler and after-boiler regions, whereas the long-chain dispersing polyamines provide extremely effective dispersing action both to incoming salts as well as Silica. In fact, the property of these polyamines of binding the Silica in the boiler water with the sludge is an important advantage of this technology as the conventional treatment has no effective solution for Silica problems in the boiler. It has been observed that on adoption of multi-component polyamine treatment the Silica levels in the boiler water are significantly lower compared to Silica present in the sludge, thus testifying to its dispersing action. It is therefore evident that even with the Silica levels incoming with the feed water remaining same, the actual Silica in the boiler water would be far lower as compared to conventional treatment.

#### **Contribution towards Energy Conservation :**

While comprehensive protection against corrsion is a major advantage of the multi-component polyamine technology, the most significant advantage specifically from the point of view of Indian conditions is substantial energy saving leading to economic gains in real terms.

The reason for the energy saving lies in drastic reduction in blowdown levels as compared to the conventional treatment. It is to be noted that in the Phosphate based treatment, blowdown of precious hot water is a controlling factor in limiting the levels of salts and Silica in the boiler, which would otherwise have a damaging effect on the entire system.

# Protection against accidental ingress of corrosion products :

Apart from providing fool-proof system protection under normal system operating conditions, the multicomponent polyamine also provides significant protection against accidental ingress of acidic water, higher levels of Oxygen and  $CO_2$  and very high levels of salts.

#### Case-1

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In one of the Scandinavian pulp mills, even in the cases of complete breakdown of deaerators, which resulted in Oxygen levels in the boiler water increase in the Fe content in water/condensate samples collected at various points, thus implying the absence of any Oxygen attack on the metal surface. This in effect proves the effectiveness of the poly-amine film.

#### Case-2

In another mill in Scandinavia which was using sea water for condensor cooling, leakage in condensate tubes have resulted in entry of sea water into the system. While in the case of normal Phosphate treatment this accident would have resulted in very hard crystalline scales - difficult to remove even with Hydrofluoric Acid wash-the multicomponent polaymine treatment resulted in the formation of soft, amorphous scales which were easily removed by water jet and Hydrochloric Acid wash.

#### Case-3

In a chemical plant in India, which was the first organisation in the country to introduce this new technology, during regeneration in DM plant the diaphragm of one of the backwash valves was ruptured leading to entry of Hydrochloric Acid into the system. The boiler was thus operating at a pH of around 3.5 for a considerable period of time before this was discovered. While in the conventional treatment, this low pH would have resulted in extensive damage to the protective magnetite layer with the boiler water becoming practically black in colour, the multicomponent polyamine treatment provided complete protection and no corrosion whatsoever was detected.

#### Case-4

In the first refinery in the country which has adopted this technology, severe problems used to be encounterd in the operation of the turbines due to deposits taking place on the blades. Even after a condensate wash, the load of a 11.5 MW turbine used to rapidly drop to about 8.5 MW within a span of 5-6 months, necessitating another turbine cleaning. Polyamine dosage was started when the load of the turbine had already dropped to around 8.4 MW. Not only was the drop in loading completely arrested, within a few weeks increase in the loading was experienced thereby proving that the polyamine was not only providing a protection against deposits, but was also, in effect cleaning away the old deposits.

#### Case-5

In a Rayon Grade pulp plant in India, using conventional treatment, the turbine had to be stopped every month for steam wash to eliminate the deposits. Since the polyamine treatment was introduced over a year ago, there has been no need to stop the turbine for any further cleaning.

#### Case-6

In a prestigeous joint-sector Newsprint mill in Southern Part of India this treatment was started in December 89. After a few weeks of the introduction it was observed that the polyamine was successfully cleaning out of the hardness deposits which had taken place during the earlier treatment. Further major energy conservation was achieved by total elimination of blowdown. On inspection, 10 months after introduction of polyamine treatment, both turbines and boiler were found to be absolutely clean.

#### Case-7

In one of the premier public sector Steel Plants, within 2 weeks of introduction of polyamine treatment blowdown levels were reduced to such an extent that the steam saved is equivalent to an extra generating capacity of 3 MW of power.

Polyamine treatment has also been successfully introduced, since March' 91 in another public sector Steel Plant for their 100 bar boilers.

The above cases have proved, in actual practice, that this technology also provides valuable petection even in situations where conventional treatment would have resulted in severe equipment damage.

### SALIENT FEATURES OF MULTI-COMPONENT POLYAMINE TREATMENT

From the above, the various features of this exciting technology can be enumerated as under :

- Formation of a smoo h, supple, monomolecular, stable polyamine protective film on all moist metal surface – preventing all corrosion attacks and safeguard agaiast deposits.
- Elimination of salt based treatment results in substantial reduction of blowdown losses. As the amine film guards against deposits, far higher levels of TDS and silica can be allowed in the boiler, thus further adding to blowdown reduction. Both these factor combined lead to significant economy of expensive fuel as well as feed water. In all cases where this technology has been introduced in this country, financial saving in real economic terms have been quite substantial.

- Dosing is done only in the low pressure side, at the suction of the feed water pump or in the deaerator, below the water level. Thus use and maintenance of the high pressure dosing pump used for dosing of phosphates is eliminated.
- \* Single points dosing, eliminating the necessity of dosing a number of chemicals.
- Use of multicomponent polyamine treatment not only results in a protective film but also cleaning of the metal surfaces where corrosion or deposits have already taken place in the past.
- \* The thin amine film replaces a far thicker oxide layer. The thermal conductivity of the amine film is also much more than that of the oxides. The combination of these two factors leads to substantial improvement in heat transfer characteristics. This is of special importance for paper mills as the increase in heat transfer results in lower steam consumption in the dryers. Alternatively the paper machine can be speeded up to an equivalent extent using the same amount of steam as before and giving higher production.

#### CONCLUSION

Traditional phosphate based treatments can be replaced by multicomponent polyamine formulations leading to comprehensive system protection increased heat transfer and substantial energy saving and improved power generation. This technology also leads to tremendous case of maintenance and significant reduction in maintenance requirement and down-time.

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