Application Note
Power No. 02

Monitoring Oxygen Scavengers in Boiler Water

Introduction

Dissolved oxygen is a prime contributor to corrosion in power plant steam cycles and the use of oxygen scavengers is one way to keep it as low as possible.

Measuring hydrazine and other oxygen scavengers with confidence avoids underdosing which risks oxygen corrosion or overdosing which increases operating costs and the risk of copper corrosion.

Highly accurate, stable and quick hydrazine measurements aid process control and plant efficiency.

Oxygen scavengers

DO_2 (dissolved oxygen) is a prime contributor to corrosion in power plant steam cycles and is affected by a number of design and chemistry related parameters. Correct plant operations and reliable instrumentation information contribute to maintain low oxygen levels. The addition of oxygen scavengers is one solution that is commonly applied to meet this goal.

There are many criteria for the choice of a specific scavenger.

The first criteria is that it should not generate solids, which can either damage turbine blades or generate deposits in heat exchangers with thermal transfer decrease. The consequence is to look first for organic, non-solid scavengers.

Other criteria of interest are:

- Quick reaction efficiency at any temperature
- No carcinogenic risk or special handling
- Good thermal stability at high temperature
- No by-products generated in the condensate circuit, promotion to the formation of a passivating metal film
- No interaction with other chemicals used, no reaction with materials
- No contribution to lowering the pH to corrosive levels (pH<8)
- Low cost

Over the years hydrazine has been considered the best choice when looking at the above mentioned criteria. Today, some plants are moving away from the use of hydrazine due to carcinogenic risks and special handling required, however many large, steam generated power plants still find great value in its use.

How oxygen scavengers work

Hydrazine
Hydrazine is an inorganic compound, a colourless flammable liquid with an ammonia like odour. It reacts in different ways:

1. Firstly, product of reaction between hydrazine and oxygen is nitrogen, which has no effect on boiler and turbine operation.
   $N_2H_4 + O2 \rightarrow N_2 + 2H_2O$

2. Secondly, the residual hydrazine, once heated above 205°C in the boiler, decomposes to ammonia which increases the feedwater pH level, reducing the risk of acidic corrosion.
   $3N_2H_4 + Heat + 2H_2O \rightarrow 4NH_3 + O_2$

3. Finally hydrazine reacts with the hematite (Fe_2O_3) layer on the boiler tubes and forms a stable and hard magnetite (Fe_3O_4) layer, protecting the boiler from further corrosion.
   $N_2H_4 + 6Fe_2O_3 \rightarrow 4Fe_3O_4 + N_2 + 2H_2O$

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Carbohydrazide
The carbohydrazide is a white crystalline solid with a melting point of 153°C. It decomposes upon melting and is highly water soluble.

1. Indirect reaction (> 180°C)
   $(N_2H_3)2CO + H_2O \rightarrow 2N_2H_4 + CO_2$
   $2N_2H_4 + 2O_2 \rightarrow 4H_2O + 2N_2$

2. Decomposition (> 200°C)
   $(N_2H_3)2CO + H_2O \rightarrow 2NH_3 + N_2 + H_2 + CO_2$

The theoretical dosage required to scavenge one part DO_2 is 1.4 parts carbohydrazide. Many of the same benefits of hydrazine are provided but without the carcinogen risk: ammonia generation with pH increase and efficient corrosion protection, magnetite creation as protective layer. For these reasons, carbohydrazide is a good alternative to hydrazine.

Dosification and measuring spots

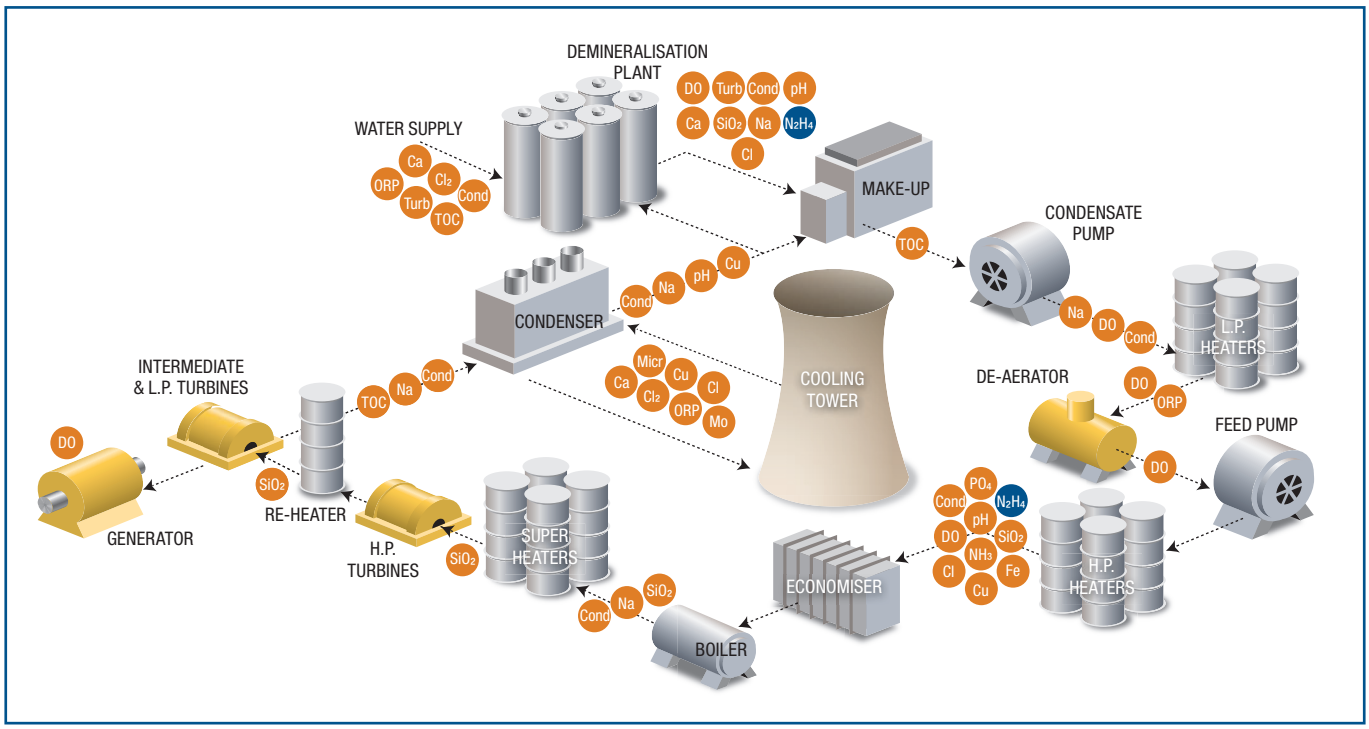
Oxygen scavengers injection and measurement are carried out where DO_2 concentrations can be found:

- Polishing plant outlet
- Condensates pump discharge. Condensate are the major source of contamination because they may be in contact with the external source of pollution (raw water) when there are condenser tube leaks.
- De-aerator outlet. Oxygen scavengers are added to the de-aerated boiler feedwater to remove the last traces of oxygen that were not removed by the de-aerator
- Economiser inlet. For optimising the efficiency of the boiler, extending its lifespan and ensuring the steam quality, quality requirements of feed water are essential. The scavenger avoids the pre-boiler corrosion risks.

The quantity of oxygen scavenger to inject is either:

- Determined from the initial DO_2 content at the deaerator outlet (before the scavenger addition). Theoretically, 1.0 ppb of hydrazine is required to react with 1.0 ppb of dissolved oxygen, however, in practice 1.5-2.0 parts of hydrazine are injected per part of oxygen. Generally $[N_2H_4]$= initial $[DO_2]$ x 3
- Fixed to obtain a minimum residual hydrazine concentration. Generally, residual $[DO_2]$ +7 to 10µg/l.

Continuous analysis of DO_2 is combined with oxygen scavenger and made on the boiler feed water, de-aerator outlet and the condensate discharge. Injection is done via dosing pumps with a solution at 35%. At temperatures below 150°C the reaction with oxygen is very slow, the use of hydroquinone as catalyst increases the reaction rate from 10 to 100 times.



Locations for oxygen scavengers monitoring

Why measuring hydrazine is so important

Injection of lower than required levels hydrazine will result in insufficient oxygen removal, further corrosion and deposition, which reduce plant efficiency.

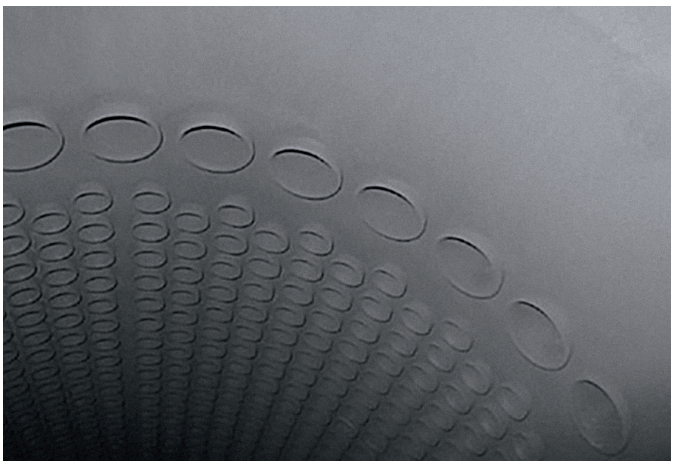
On the other hand increasing the hydrazine injection too much will lead to other problems:

- The first being a cost increase without any recovered benefit.
- The second, an accelerated corrosion of copper with deposition in the boiler and on turbine blades.

Hydrazine which does not react with oxygen by the time the water leaves the de-aerator will quickly decompose to ammonia in the High Pressure heaters.
Where ammonia and copper meet, there is potential for copper corrosion and generation of a copper-ammonia complex [1]. This may occur at any copper-alloy condenser, feedwater heaters or other component.
The copper-ammonia complex travels through the feedwater system into the boiler until it becomes unstable. The ammonia volatilises and the copper finds the nearest surface on which to precipitate as pure copper metal. From a boiler tube, super-heater tube or a high pressure turbine blade.

Another type of copper corrosion is created during shutdown: copper oxides that are created and sloughed off the surface during start-up, and ammonia-copper corrosion by-that are created by an excess of hydrazine or amine. [2]

All these deposits affect the efficiency of the turbine and of the plant.



A stable magnetite layer inside a boiler ($Fe_3 O_4$ with a dull black or gray appearance)

Boiler at Rawhide power plant, USA.

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The solution from HACH LANGE: POLYMETRON 9586 Oxygen Scavenger Analyser

Monitor Hydrazine and Carbohydrazide
The POLYMETRON 9586 Oxygen Scavenger Analyser is suitable to monitor the level of hydrazine and other oxygen scavengers such as carbohydrazide in power plant boiler feedwater. Determining the optimum level of oxygen scavenger to add to the boiler feedwater will help avoid problems of corrosion due to dissolved oxygen.

Fast Response Time
The analyser provides continuous measurement with a 90 % response time in less than one minute. This allows the accurate dosing of chemical additions in feedwater and ensures cost effective operation.

Unique Operation
Unlike the traditional amperometric techniques that use two electrodes, the 9586 Oxygen Scavenger Analyser uses three electrodes; One platinum working electrode (anode), one stainless steel counter electrode (cathode), and a reference electrode of Ag/AgCl.
During operation, the voltage between the platinum anode and the reference electrode is maintained using a potentiostat. Voltage drift due to changes in the sample composition or flow are eliminated thus resulting in a better measurement accuracy.

Self-Cleaning Electrodes
Teflon® beads, driven by the sample flow, circulate on the surface of the platinum electrode to prevent deposits.
This reduces maintenance costs and analyser downtime.

Inexpensive to Operate
Reagent consumption is very low so replenishment is only required every four weeks. Re-calibration, by comparison method, is only needed once per month. The working electrode is self-cleaning and there are few moving parts and pumps. Routine maintenance usually requires about 15 minutes per month.

System configuration

The Polymetron 9586 Oxygen Scavenger Analyser is shipped on a complete panel with controller, probe, cable, flow cell and all hardware necessary for installation. Power supply options: without cord, 115-240 VAC or 7-24 VDC.

References

[1] D. Daniels and J. Latcovich, Copper deposits on turbine blades: a copper plated thief, Hartford Steam Boiler

[2] B. Dooley and K. Shields, Alleviation of Copper Problems in Fossil Plants, Materials and Chemistry, EPRI, Palo Alto, California

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