Troubleshooting corrosion of a high-pressure water-steam cycle in a heavy chemical industry

Success story with Adicontrol technology

D. Gutiérrez, N. Ramos, P. Infante, C. Sanabria, M. C. Royo, N. Adroer and J. Aumatell ADIQUIMICA

Based on the recommendations made by the EPRI (Electric Power Research Institute) and IAPWS (International Association for the Properties of Water and Steam) organisations for high pressure watersteam cycles, the company Adiquimia presents its Adicontrol technology, which provides effective corrosion protection for the metal surfaces of the entire high pressure water-steam cycle.

KEY WORDS: Corrosion; High pressure water-steam cycle; Heat exchangers; Adicontrol.

Based on the recommendations that the organizations EPRI (Electric Power Research Institute) and IAPWS (International Association for the Properties of Water and Steam) make for high pressure water-steam cycles, the company Adiquimia presents its Adicontrol technology, which allows achieve effective anti-corrosion protection of the metal surfaces of the entire high-pressure water-steam cycle.

KEYWORDS: Corrosion; High pressure water-steam cycle; Heat exchangers; Adicontrol.

INTRODUCTION HIGH PRESSURE WATER-STEAM CYCLE

The high-pressure water-steam cycle is an industrial process with at least one of the following two objectives:

- Transferring heat energy to a given production unit.

- Transforming the heat energy contained in the steam generated into kinetic energy which, in turn, will be transformed into electrical energy by means of an alternator coupled to the system's steam turbine.

PROBLEMS ASSOCIATED WITH WATER CHEMISTRY IN

A high-pressure water-steam cycle is decisive in the correct operation of this type of system, especially those whose objective is the generation of electrical energy from the conversion of the kinetic/mechanical energy contained in the superheated steam generated. To this end

Indeed, international organisations such as EPRI (Electric Power Research Institute) or IAPWS (International Association for the Properties of Water and Steam) and others have developed "good practice" guides that take the empirical knowledge gained in real water-steam cycles and translate it into recommendations and limits to be maintained for certain physicalchemical parameters of water/steam.

These recommendations aim to standardise the water chemistry in this type of systems to protect them against chemical or flow-accelerated corrosion (FAC) processes, and to avoid the transport of chemical compounds with the steam to prevent their deposition in other parts of the system, mainly in the turbine, which could cause damage to the turbine, as well as significant losses in performance.

A water-steam cycle presents problems common to any system where water comes into contact with metallic surfaces of different compositions. However, these are exacerbated by the extreme operating conditions in terms of pressure and temperature. Additionally, the inclusion of critical elements in the process, such as turbines. superheaters and condensate, make a water-steam cycle а system particularly sensitive to water quality, both in liquid and vapour states.

Given the current pre-accession processes, the water treatment in steam generation plants, the main corrosion problems on heat transfer surfaces are due to the deposition of metal oxides (mainly iron) on the surfaces [1].

"The main corrosion problems on heat transfer surfaces are due to the deposition of metal oxides.

One of the first consequences of the formation of such deposits, in addition to the development of corrosion problems, is that they act as insulators and cause overheating of the heat transfer surfaces. For example, in the case of

of haematite ($_{Fe2O3}$) and magnetite ($_{Fe3O4}$), the heat transfer coefficient can be as high as 80

times less than that of carbon steel. It is important to ensure that the boiler water is treated, as this is important to ensure that the rate of deposition and agglomeration of iron particles on the heat transfer surfaces is slowed down.

The main factors to be taken into account for optimal operation of the water-steam cycle can be summarised in the following points:

• Entry of contaminants with the make-up water into the cycle. Certain chemical species, present in the generator water as dissolved or colloidal solids, can be transferred to the steam through selective vaporisation processes, causing corrosion. exfoliation and/or deposition problems, reducing their nominal performance [2-4]. Silica is of the most problematic one contaminants in water-steam cycles, because it forms very adherent incrustations inside boilers and turbines, its entrainment potential increases with increasing vapour pressure, and it can very easily enter a steam system. Sodium is another pollutant that causes problems in boilers, because it is the main cause of many corrosion processes. Therefore, it is important to monitor the water in water-steam cycles. The quality of the

water at the outlet of the pretreatment can be evaluated in terms of its specific conductivity. The cation conductivity represents one of the most relevant indices in the operation of a water-steam cycle, and it is usually monitored with continuous meters at the different points of the water-steam cycle.

• The pH of the cycle water. The pH values at all points are determined according to the manufacturer's recommendations and the type of chemical treatment. Adequate pH values allow to operate in optimal conditions from the point of view of minimising corrosion phenomena on the metal surfaces.

 Dissolved oxygen levels in the cycle water. Oxygen can be considered to be the driving force of corrosion, and for this reason great efforts are made to prevent its presence in boiler water. Dissolved oxygen must be removed by thermal degassing of the feed water, and this action must be completed by the addition of reductants that destroy the traces of oxygen still present in the solution. Therefore, although the degassing equipment present in the cycle is responsible for the elimination of most of the residual dissolved oxygen in the water, it is necessary to refine this elimination in order to reach the values recommended in the corresponding standards and guidelines. In any case, it is interesting to remember that the protective layers are the product of the oxidation of the metal, at a value lower than the maximum. If the oxidation these progresses, protective layers no longer form and the corrosion progresses driven by the oxidising medium.

CASE STUDY OF AN EPISODE OF UNDER DEPOSIT CORROSION IN HEAT EXCHANGERS OF A HEAVY INDUSTRY PLANT DESCRIPTION OF THE PLANT

The present study describes the solution adopted by Adiquimica to solve an episode of corrosion under deposit in the heat exchangers of a chemical industry plant. Figure 1 shows the flow diagram of the plant's water-steam cycle. In the following, the characteristic elements of the plant are detailed:

- Water pre-treatment system, or unit operations to condition make-up water to compensate for system losses (blowdowns applied to the system, non-condensed steam or nonrecovered condensate).

- Degasser, or system for the removal of dissolved gases by contact of the feed water with low-pressure steam. The characteristic parameter of a deaerator is its performance in removing dissolved oxygen from the water, which is mainly responsible for the oxidation of the metal water circulation lines.

- Boiler, or water vaporiser by heat transfer from the combustion of the fuel used in the plant. According to the classification established by the international body EPRI (Electric Power Research Institute) [5, 6], the boiler is considered to operate at high steam generation pressures because it operates above 40 bar 600 (approximately psi). and therefore subject to the recommendations set by that body.

- Condenser, between the steam leaving the heat exchanger tubes and the system's cooling water (itself cooled by an evaporative cooling device). This element, operating under vacuum, is intended to condense the steam for maximum utilisation of the plant's resources. "This study describes the solution adopted by Adiquimica to solve an episode of corrosion under deposit in the heat exchangers of a plant in the heavy chemical industry.

FIGURE 1. Flow diagram of the main elements of the case study water-steam cycle

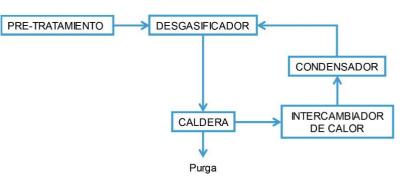
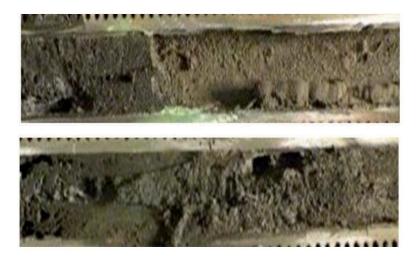






FIGURE 3. Heat exchanger tubes blocked due to high deposit build-up



UNDER TANK CORROSION PROBLEMS BEFORE ADIQUIMICA'S INTERVENTION

Before Adiquimi- ca's intervention, one of the plant's heat exchangers was found to be clogged and its tubes deformed.

The following problems occurred in the water-steam cycle, which led to additional production stoppages in addition to those programmed, with their associated costs, both in terms of materials to be replaced and temporary cessation of production activity:

- Under deposit corrosion on heat exchanger tubes. The affected tubes experienced a loss of thickness due to corrosion which caused a leakage. Figure 2 shows the tubes affected by the corrosion phenomena.

- High build-up of deposits in the inlet manifold and in the heat exchanger tubes. Deposits pro-

The corrosion of the metal surfaces of the water-steam cycle. Figure 3 shows the blocked heat exchanger tubes.

The cause of the corrosion under the tank was the inadequate treatment and lack of control of the critical parameters of the watersteam cycle before Adiguimica's intervention. The pH of the boiler and condensates was between 5 and 6 pH units. Figure 4 shows the pH values before Adiquimica's intervention. The average pH was pH=5.74 in the boiler and pH=5.81 in the condensate. In order to operate under optimal conditions from the point of view of minimising corrosion phenomena of the metal surfaces, pH values of around 9.2 units are recommended at all points of the water-steam cycle. Therefore, the low pH values in the water-steam cycle promoted corrosion phenomena.

of the metal surfaces. As a consequence of the high corrosion experienced by the installation, high levels of iron were detected in the boiler and condensate. Figure 5 shows the iron values before Adiquimica's intervention. The average iron concentration was 5,000 ppb in the boiler and 1,000 ppb in the condensate.

IMPROVEMENT ACTIONS FOR THE CONTROL OF THE WATER-STEAM CYCLE ADIQUIMICA SOLUTION

In order to maintain the maximum performance of the water-steam cycle and to avoid the phenomena of corrosion of the cycle and the accumulation of deposits in the exchanger, Adiquimica implemented the following improvement actions:

Optimised chemical treatment.
Implementation of Adicontrol technology for the water-steam cycle.

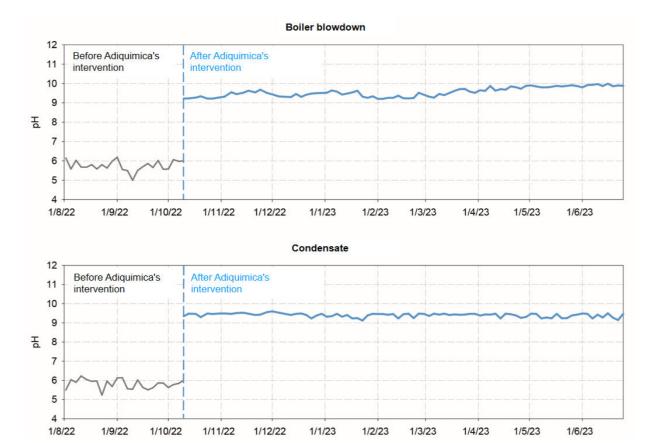


FIGURE 4. pH evolution in the boiler blowdown and in the condensate before and after Adiquimica's intervention.

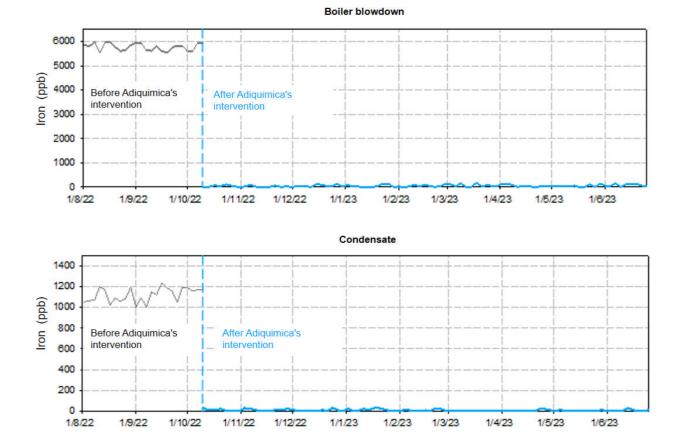


FIGURE 5. Evolution of iron concentration in the boiler blowdown and condensate before and after Adiquimica's intervention.

OPTIMISED CHEMICAL TREATMENT OF THE WATER-STEAM CYCLE

A treatment based on oxygen reducer, volatile alkaliniser and generator water alkaliniser was implemented, with the following objectives:

- Reduction of residual oxygen in feed, steam and condensate lines.

- Alkalinisation of the alimentation and condensate lines.

Both treatments are based on the use of compounds with zero salt content and of a volatile nature, in order to act at all points of the cycle, even if they are dosed in the feed line after the degassing operation.

The oxygen reductants used also have a passivating effect, i.e. they allow the non-protective oxide surface layers to be trans- formed into magnetite or protective mixed iron oxides. Given the volatility of the reducers used, this function is maintained in the feed, steam and condensate lines, providing complete protection of the circuit.

The alkalinising compounds used are based on mixtures of neutralising volatile compounds with two distinct functions:

- Neutralisation of CO₂ from the thermal decomposition of the carbonaceous species contained in the make-up water.

- pH increase without substantial increase in the salt load of the water.

The alkalinisation of the generator water, while promoting the formation of a buffer at pH around 9.2 units, aims to neutralise possible pH decreases caused by disturbances in the water supply. occurrences in the cycle, such as possible contamination by low molecular weight organic compounds, degradation of treatment products etc.

ADICONTROL TECHNOLOGY FOR THE WATER-STEAM CYCLE

The water-steam cycle is critical to the plant's production efficiency. Therefore, optimal an and customised water treatment of the water-steam cycle is important to maintain the efficiency of steam production. Adicontrol is а technology developed entirely by quimica that allows Adian integrated and reliable control of our water-steam cycle treatments. It provides the security of knowing that the installations are controlled, saving water, energy and money.

Our experience in dealing with The development of high-pressure water-steam cycles and constant innovation enable us to offer a solution that is The Adicontrol technology was designed specifically for the needs of the plant, monitoring system conditions and the performance of the water-steam cycle in real time. Adicontrol technology was designed specifically for the needs of the plant, monitoring system conditions and the performance of the water-steam cvcle in real time. Adicontrol technology implements an expert control and support system tailored to Industry 4.0, resulting in improved process efficiency, productivity and profitability. It improves process performance, controls corrosion, keeps surfaces clean and reduces water and energy consumption. The results enable sustainability goals to be met with continuous steam production and system protection, reducing operating costs and CO emissions₂.

Adicontrol is linked to a being.

The monitored data are evaluated by means of scenario analysis and artificial intelligence. The monitored data are evaluated by means of scenario analysis and artificial intelligence that allow the for integrated management the of information and learning of the behaviour of patterns each installation. It generates reports on key process indicators (KPIs). It has an advanced alarm system in the event of a deviation. It is an active service 24 hours a day, 365 days a year. Allows online visualisation of the

information from the web on any device.

Our team of technicians and experts constantly manages the information relevant and kev aspects of the installation to make an accurate diagnosis of the process status, make recommendations to aid decision-making, optimise and adapt performance dynamically. intervene before the problem occurs, take immediate action in response to alarms and deviations, and resolve complex situations.

RESULTS OF IMPROVEMENT ACTIONS

The implementation of optimised treatment and Adicontrol technology allowed the water-steam cycle to operate at the recommended values of the critical plant parameters set by the EPRI guidelines [5, 6]. Corrosion problems on the heat transfer surfaces were eliminated. Figures 4 and 5 show the pH and iron values in the boiler and in the condensate, after applying the improvement actions proposed by Adiquimica. The pH increased and stabilised at the recommended values above 9.2 units. And iron levels were reduced to an average of 57 ppb and 3.5 ppb in boiler and condensate, respectively, indicating that effective corrosion protection of the metal surfaces was achieved

CONCLUSIONS

implementation The of an chemical optimised treatment and the Adicontrol technology achieve an integral control of the high-pressure water-steam cycle, allowing operation according to the recommendations of the EPRI (Electric Power Research Institute) and IAPWS (International Association for the Properties of Water and Steam) organisations, in relevant parameters such as pН and conductivity, corrective avoiding interventions minimising and operating costs.

Chemical treatment based on The oxygen reducer, volatile

alkaliniser and alkaliniser of the generator water provide effective anti-corrosion protection for the metal surfaces of the entire highpressure water-steam cycle.

Adicontrol technology monitors system conditions and water-steam cycle performance in real time, improves process efficiency, controls corrosion, keeps surfaces clean, and reduces water and energy consumption. The results enable sustainability goals to be met with continuous steam production and system protection, reducing operating costs and CO emissions₂

Bibliography

[1] A. Ramesh, N. Laycock, P. Shenai, A. Barnes, H. Van Santen, A. Thyagarajan, A.

M. Abdullah, and M.P. Ryan. Critical Deposit Loading Thresholds for Under Deposit corrosion in Steam Generators. Science Section, Vol. 78 (2022)

[2] I.F. Wright, P.F. Tortorelli, and M. Schütze. Oxide Growth and Exfoliation of Alloys Exposed to Steam. EPRI Report No. 1013666 (2007).

[3] I.G. Wright and R.B. Dooley. A review of the oxidation behavior of structural alloys in steam. International Materials Reviews, 55 (3), 129-167 (2010).

[4] Daniel, P.L., Durisaile, J.C., Watage of Economizer Inlet Header Tube Stubs. The Babcock & Wilcox Compan, Barberton, OH, U.S.A., 186-4019 (1993).

[5] Electric Power Research Institute. Cycle Chemistry Guidelines for Combined - Cycle/ Heat recovery Steam Generators (HRGs), Palo Alto, CA:2006. 1010438

[6] Electric Power Research Institute. Interim Consensus Guidelines on Fossil Plant Cycle Chemistry. Palo Alto, June 1986. CS-4629.

"The implementation of optimised chemical treatment and Adicontrol technology achieves comprehensive control of the high-pressure water-steam cycle.