PREDICTIVE ACID CHEMICAL CLEANING OPERATION (PACCO©) AN INNOVATIVE METHOD TO REMOVE IRON OXIDE DEPOSITS IN THE SECONDARY SIDE OF STEAM GENERATORS (SG)

Steam Generators (SG) usually present important deposit loading and Tube Support Blockage, resulting from Secondary Side corrosion products. These phenomena modify SG behavior which can lead to safety, heat Exchange performance and lifetime problems.
In this context, a Chemical Cleaning Process (PACCO) was designed by GDES to solve the issue.
After almost two years of intensive lab tests , pilot simulation and mock-ups , the chemical process was finally qualified by EDF.
The aim of the work was firstly the development in laboratory of a chemical process that could eliminate partially the deposit loading, respecting the integrity of materials and gas emission limits. Secondly, the objective was the design and the implementation of the process on-site. The process has been applied successfully in 6 SG in Dampierre 1 and 2 nuclear power plants in France.

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Steam generators in pressure-water nuclear power plants, usually present deposit loading and tube support clogging and fouling over time due to the deposition of corrosion products resulting from the secondary circuit. Indeed, during plant operation, corrosion products find their way into the secondary fluid and tend to concentrate in the SG, which can led to accelerated corrosion of the structural components.

The main problem presented by steam generators is the degradation of the tubes. The main degradation mechanisms that have affected the generator tubes are: denting and stress corrosion cracking on the primary side (PWSCC), denting and stress corrosion on the external diameter (ODSCC), friction wear (Fretting), High cycle fatigue, strangling (Denting), pitting and accumulation of deposits.

The materials and methods used in the manufacture of the components of the steam generator affect their susceptibility to corrosion, especially to the formation of cracks due to stress corrosion. The degradation of the tubes is also influenced by other aspects of the design and manufacture of the steam generator, such as the design of the tube support sheets and the method of installation.

After several cycles, this deposit's accumulation (metallic oxides as magnetite, zinc oxide and metallic copper) can also led to a loss of heat exchange of the unit and consequently to a decrease of electric power production of the plant.

The obstruction of the free parts constitutes the main mass of the deposits present in the steam generators. These fouling and clogging phenomena modify the thermo-hydraulic and vibratory behavior of steam generators with consequences in terms of safety, reactor performance and life-time potential. The deposits are located mainly in the following parts of the secondary side of a Steam Generator:

- On the different sheets in the form of sludge that can form locally very hard shells,

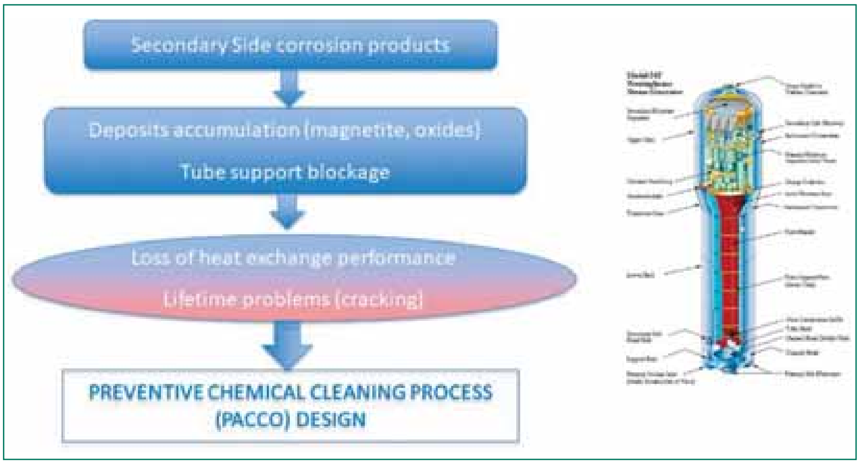

Figure 1. Origin of the PACCO process.

Figure 2. Chemical analysis lab.

- In the area of circulation of the tubes,
- In the common zone of the secondary elements of the Steam Generator (vessel, beam envelope, etc.)
- In the spaces (interstices) located between the tubes and the sheets until they fill them completely
- In the foliar steps of the water sheets until completely closing them.

In this context , a preventive chemical cleaning process (PACCO©) has been designed by GDES and Comex Nucléaire with the purpose to partially eliminate the SG secondary side deposits of EDF NPPs guaranteeing its operation for several cycles and ensuring near-manufacturing performance (Figure 1).

The process can be applied on all the EDF SGs with a deposit loading range between 500 and 4000 Kg per SG, containing up to 8% of copper and up to 10% of zinc oxide.

PACCO© process design was carried out in three steps:

- Chemical process development (Figure 2).
- Qualification process in mockups (Figure 3).
- Design of the equipment.
- Implementation on site : Dampierre 1 NPP in 2013 and Dampierre 2 NPP in 2015 (Figure 4).

PROCESS DESCRIPTION

PACCO© is a dynamic process performed with recirculation and sparging that can allow a better homogenization of the solution and a better

Figure 3. Laboratory test mockup.

Figure 4. Chemical analysis lab facilities.

efficiency than other process in the market. The duration of the whole process is short (less than 3 days per SG) and it is possible to carry out the cleaning of two SGs in parallel. The draining phase is very efficient as designed and verified during the first operation in Dampierre 1:2 hours in a nominal mode and less than 4 hours in failure mode. The chemicals used are CMR ("Carcinogenic, Mutagenic, Reprotoxic") free, totally harmless and environmentally friendly.

The process consists of two main phases: an acid phase followed by a copper elimination phase (Figure 5).

The acid phase refers to a partial magnetite deposits removal at low temperature (between 30 to 45 °C) by using a combination of organic acids: citric acid plus an organic reductive agent at low concentration. The chemical cleaning is carried out by recirculating the solution through the SG secondary side and nitrogen sparging in order to keep reductive conditions, minimize corrosion phenomena and ensure the homogenization of the solution through the SG.

The optimum pH range for magnetite dissolution occurs between 3.2 and 4.8. Therefore, the complex citrate-ammonia is known to be better complexing agent of magnetite than citrate ion and is used in many chemical industrial applications. Then ammonia is part of the acid phase and used to adjust the pH between 3 and 4.

Corrosion inhibitor and antifoam are also added in order to respectively, minimize corrosion and prevent from foam formation.

The second phase of the process is a copper elimination step with the aim to eliminate metallic copper initially present in the SG deposits or copper resulting from copper-plating phenomenon occurred during the acid phase.

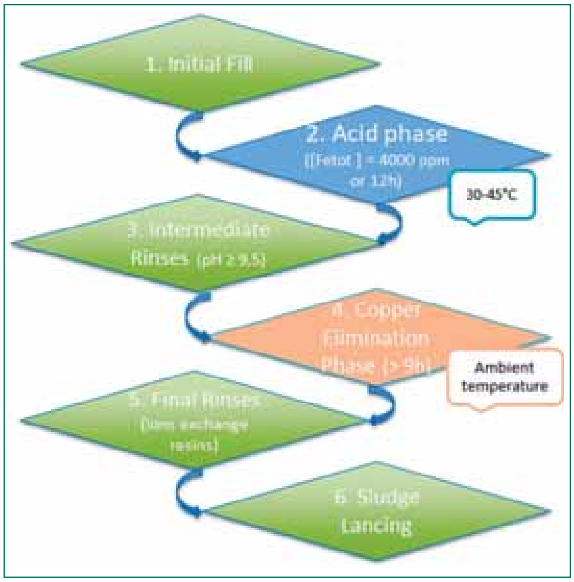

Figure 5. PACCO Process main steps.

This phase is performed at room temperature, using ammonia as a complexing agent, and a strong oxidizing agent, hydrogen peroxide, injected with a controlled flow rate in order to avoid any uncontrolled temperature elevation and optimize oxidation.

First, the hydrogen peroxide combined with the oxygen provided by air sparging, enables the copper oxidation into cupric ions. Then, a complex of copper ammonia ($Cu(NH_3)_4^{2+}$) results from the reaction between tne cupric ions and ammonia. As this complex is very stable at basic pH, the elimination of copper by ammonia is easily achieved by the addition of basic buffer agent.

PROCESS IMPLEMENTATION

The implementation of the chemical cleaning process is divided into six steps:

1) Initial filling and leak and heat tests of the circuit.
2) Acid phase: dissolution of metallic oxides, mainly magnetite.
3) First rinses: elimination of acid residues by rinsing with small and full volumes series.
4) Copper elimination phase.
5) Final rinses: small and full volume.
6) Sludge lancing to remove the hard deposits on the tube support plate.

The end of the acid phase is established by a chemical criterion based on iron dissolution that ensures a good cleaning efficiency (Figure 6) and a minimum of corrosion: some thousand of ppm or a maximum duration (less than 16 h) for the low charged SGs. A rinse step is the set off to eliminate the acid residues and to prepare the system for the next step.

The end of the copper elimination phase is determined by the criterion of duration (< 9h).

The end of the final rinse phase is achieved when the conductivity is less than 30µS/cm. This criterion guarantees the complete cleaning of the solution residues and also leaves the SG as clean as possible before restarting the SG operation.

During the implementation of the project in Dampierre 1 NPP a kind of colored black solid deposits have been noticed in one of the SG cleaned . After a thorough research it was determined that the root cause of those deposits was related to the interaction between the Dibutil-thiourea present in the corrosion inhibitor and the copper in solution. Several tests have been performed with different corrosion inhibitors until the most suitable has been proved to be more efficient without any production of black deposits.

A new procedure called PACCO Bis has been set up introducing the new inhibitor and testing its efficiency and harmlessness. As a result of that development only the acid phase was modified, keeping the same conditions for the copper removal phase.

It has been taken advantage of those tests to qualify the new procedure with a unique range of deposits concentrations, between 4 and 10 g/l.

Finally PACCO Bis was implemented in Dampierre 2 NPP in July 2015 with similar success than in Dampierre 1.

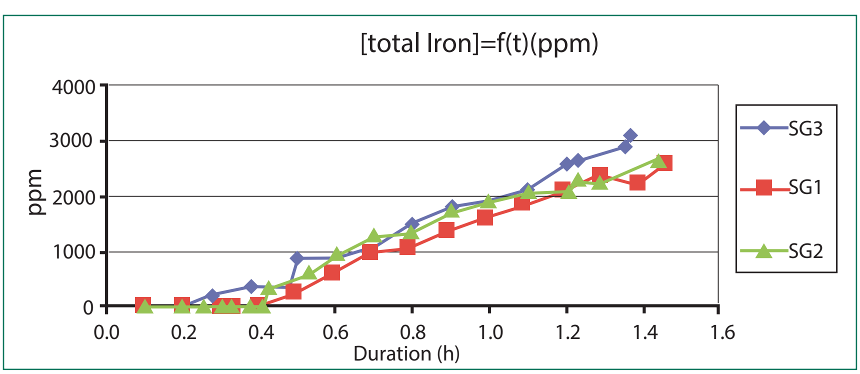

Figure 6. Chemical process monitoring.

RESULTS

By implementing this method on-site (Dampierre 1 and 2) the results in terms of efficiency was 300 Kg of deposits per SG removed which represents around 40% of the initial deposit load (Figure 7).

Corrosion was estimated by a reliable on-line corrosion monitoring system (CMS) as Figure 8 shows. The general corrosion was under the required limits (100 µm): <21 µm for caron steel, low alloy steel and welded materials, free and galvanic corrosion less than 0,1 µm for stainless steel and inconel.

The main gas effluent released into the atmosphere was ammonia. The estimated amount was approximately 15 kg for the 3 SGs, so there is no relevant impact in the environment. The total amount of liquid effluent is around 1400 m^3 that will be treated by a French waste management company.

	SG1	SG2	SG3
Maximum free corrosion (µm)	3,6	2,1	4,3
Maximum galvanic corrosion (µm)	18,6	18,6	20,6
Total amount of deposit removed (kg/SG)	**270**	**289**	**347**
% efficiency (total amount of deposit removed / estimated initial deposit loading) *Initial deposit loading: 922kg	**30**	**31**	**38**

Figure 7. Results for Dampierre 1.

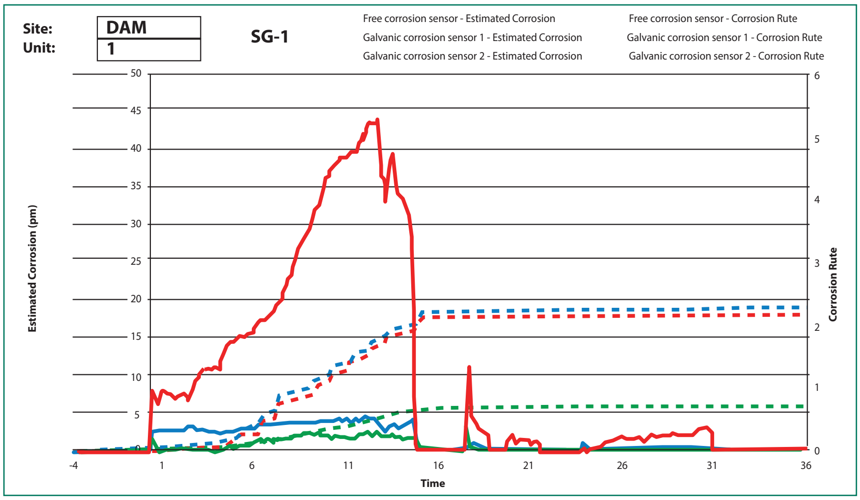

Figure 8. Online corrosion monitoring.

CONCLUSIONS

This PACCO chemical cleaning operation in French NPPs have been carried out successfully and have complied with the corrosion and efficiency criteria defined by EDF. PACCO has demonstrated its capacity to eliminate around 40% of the initial deposits loading maintaining the SG integrity with a minimum of gas emission.

The complementary skills of Comex Nucléaire and GDES, combining nuclear and chemical know-how, has led to the success of the operation managed by a multicultural and committed teamwork.

GDES has developed a new chemical procedure that has been applied with great success in 6 steam generators in French NPPs, becoming a powerful alternative to the existing methods in the market.

With this innovative method GDES continues to diversify its services and activities, building on its experience and investments in R&D+I.

The main objective is to guarantee our clients an optimum efficiency in their facilities, and thus maximize the return on their investment.