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Effects of curative and preventive chemical cleaning processes on fouled steam generator tubes in nuclear power plants

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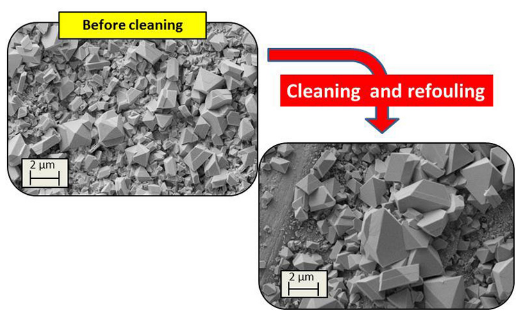
HIGHLIGHTS

- Experimental loops to study the oxidation, fouling, cleaning and refouling of steam generators.
- First study of chemical cleaning impact on SG tubes reactivity.
- Effectiveness of a curative and two preventive industrial chemical cleanings.
- Cleanings increase the porosity of the redeposited magnetite layers.
- Innocuousness of the cleanings for the Inconel tube passive layer.

GRAPHICAL ABSTRACT



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ABSTRACT

Magnetite (Fe_3O_4) deposits in the secondary circuit of nuclear pressurized water reactors (PWRs), lead to the fouling of the steam generators (SG) which decreases their thermal performances and increases the risk of corrosion of the SG tubes. As a counteraction, preventive and curative chemical cleanings (CCC) are industrially implemented to remove oxides sludges and deposits in SGs. The use of chelating agents in chemical cleaning processes could affect the passive layer of SG tubes, and modify their surface reactivity. In order to better understand these phenomena, two experimental loops have been designed and operated: the FORTRAND loop to perform and investigate SG tube oxidation, fouling and refouling and the ECCLIPS loop used to investigate the effects of the chemical cleanings.

A three steps strategy has been implemented as follows: (i) reproducing magnetite deposits on oxidized SG tubes, (ii) applying three different industrial chemical cleaning procedures (a curative and two preventive ones) and (iii) studying the redeposition (refouling) of magnetite. The fluid physico-chemical conditions upon these steps have been thoroughly followed and controlled.

Magnetite deposits formed on the SG tubes upon the first fouling have been characterized by scanning and transmission electron microscopies (SEM and TEM) and X-ray diffraction (XRD). They are shown to be composed of a dense layer of small magnetite crystals. Secondly, three different SG industrial cleaning processes were reproduced. Their timing and thermo-chemical conditions were strictly respected and they were found to dissolve most of the fouling deposit. Disperse magnetite crystallites were present on the tube surface. Moreover, TEM cross-section images showed that no general attack of the tube passive layer occurred.

Finally, the cleaned tubes were fouled again in the FORTRAND loop using the same experimental conditions as for the first fouling step. It could be concluded that chemical cleanings have no effect on the fouling kinetics of the SG tubes for a short one month period and that the amount of deposit formed

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before and after the cleanings was identical. The small crystallite dense layer observed before cleaning was not present on refouled tubes and the size of the crystallites was bigger after the cleanings. For a short time period, this morphology could result in the formation of a fouling deposit with more porosity. As the increase of deposit porosity can impact the thermal transfer at the SG tube surface, morphological changes, hardly predictable, could be important for the SG thermal performance after chemical cleaning. For a longer period, frequent SG cleaning applications should prevent the densification of the deposit and thus delay performance loss over time. To the best of our knowledge, this experimental program is the first study of chemical cleaning impacts on SG tubes reactivity.

1. Introduction

Corrosion products generated in the secondary circuit of nuclear Pressurized Water Reactors (PWRs) are transferred by the water flow from the feedwater to the steam generators (SG). The deposition of these corrosion products leads to SG fouling. They can be deposited in a loose form or as agglomerates, and are non-uniformly distributed. These deposits not only reduce the efficiency of the SG by decreasing the heat transfer, but may also enhance the risk of the corrosion of the SG tubes and the blockage of the tube support plates (Fujiwara et al., 2004; Kawamura et al., 2005, 2006). Chemical cleanings of the SGs of the Électricité de France (EDF) fleet started in 1989, and have become the priority strategy to remove oxide deposits from the SGs since 2006. Five chemical cleaning processes have been implemented up to now to restore the heat transfer effectiveness of the SGs. Among these processes, two are called "curative chemical cleanings" (CCC), using harsh physico-chemical conditions in order to recover the nominal safety operating conditions of the SGs and three are called "preventive chemical cleanings" (PCC), using softer conditions in order to prevent the consequences of an excessive fouling and of the blockage of the tube support plates (partial or complete blocking of the Tube Support Plates (TSPs) by the corrosion products).

Although the chemical nature of the deposits depends on the nature of materials used in the secondary circuit, it mainly consists of magnetite (about 80%) (Varrin, 1996). All chemical cleaning processes are designed to remove the fouling deposit by dissolution. They are based on a combination of one or more dedicated steps for removing the two main compounds of the deposit: magnetite and copper. These steps require the presence of a chelating agent to enhance the dissolution but the chelating agents used in chemical cleaning processes may affect the passive layer of SG tubes made of a nickel based alloy (Inconel 600 TT or 690 TT), and then may modify their surface reactivity. To investigate this impact, a three stage research and development program has been developed: (i) reproduce the deposits on SG tube surfaces using several techniques, (ii) apply chemical cleanings and (iii) study the redeposition of magnetite.

Two specific test loops have been designed to conduct this study. The formation of the oxide deposits on the SG tubes and the oxide redeposition have been reproduced in a loop called "FORTRAND". On the other hand, the effects of chemical cleanings on these deposits but also on SG materials have been reproduced in a loop called "ECCLIPS". Step (i) and (iii) of the study were performed in the FORTRAND test loop where corrosion products formation and deposition on SG tubes were reproduced under the nominal operating conditions of the feedwater system of the secondary circuit. In the ECCLIPS test loop, one CCC and two PCC have been investigated on fouled tubes by reproducing the cleaning processes physico-chemical conditions and fouled SG characteristics. At each stage of the study, the oxide composition and properties were determined by surface characterizations and desquamation experiments. Comparison of the oxide deposits before and after the cleaning tests have highlighted the impact of the chemical cleaning procedures on tubes surface reactivity and SG material integrity.

2. Experimental section

The experiments were conducted as follows. To reproduce the characteristics of the initial SG tubes surface in Nuclear Power Plants (NPP), a preliminary static pre-oxidation step was operated in the FORTRAND autoclave to form a passive layer at the SG tube surface. Then, the tubes were fouled *in-situ* by fluid recirculation in the FORTRAND test loop. This step is called the "fouling step". Secondly, the fouled tubes were chemically cleaned in the dedicated ECCLIPS test loop. Finally, in the "refouling step", the cleaned tubes were fouled again in the FORTRAND loop using the same experimental conditions as for the initial fouling step.

The experimental conditions and the main test loop characteristics and operations are presented below. Analysis techniques and tools employed to characterize SG tube surfaces are also described in this section.

2.1. FORTRAND loop test: SG tubes fouling study

2.1.1. Experimental loop description

The FORTRAND (FORmation and TRANsport of Deposits) loop was originally designed to study the formation and transport of corrosion products in pipes representative of the feedwater system in PWR NPP (Delaunay et al., 2011). It has been adapted to reproduce the formation of oxide deposits on the external surface of SG tubes. This experimental facility, shown in Fig. 1, is composed of three main parts working in a one phase flow:

- A carbon steel pipe section which simulates the conditions in the secondary circuit feedwater system. This section is composed by carbon steel tubes, is 21 m long and can be heated up to 250 °C.
- An autoclave made of stainless steel, which contains 12 Inconel SG tubes (90 cm in length and 19.05 mm in diameter) equipped with heating rods inserted inside the tubes, able to warm the solution up to 280 °C.
- The feedwater conditioning section is made of stainless steel and is composed by functional elements (injection tank, high pressure (HP) pump, heat exchanger, heater, cooler, backpressure regulator).

This experimental loop has been designed to reproduce the *in-situ* oxide formation and deposition on SG tubes surface. Soluble and solid corrosion products are formed by flow accelerated corrosion of carbon steel tubes in the pipe section and are driven toward the autoclave where they form a fouling deposit at the surface of the SG heated tubes.

To follow the iron concentration and speciation, both low and high temperature (up to 275 °C) samplings were done at different