

**COMPREHENSIVE INVESTIGATION OF CORROSION
PHENOMENA IN NUCLEAR STEAM GENERATORS**

Thesis of the PhD dissertation

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2006.**

INTRODUCTION, AIMS

In accordance with international trends, the life-cycle prolongation of the nuclear reactors of type VVER-440/213 at Paks NPP is a fundamental issue in the energy policy of Hungary. In the enhancement of the power capacity and/or a possible extension of the life-cycle, the contamination and corrosion state of the steam generators (SG) of the VVER 440/213 type pressurized water reactors are considered as being one of the decisive factors. The design of these energy production units, however, does not allow the replacement of horizontal SGs to be considered. Therefore, the replacement of even one SG would result in unacceptably high production loss and investment cost.

Some years ago, the primary and secondary circuit water chemistry data, and the corrosion effects of the chemical decontamination procedures performed at NPP Paks, made it clear that an overall estimation of the corrosion state of the steam generators, i.e. the preparation of a so-called “corrosion map” is inevitable. This ‘corrosion map’ takes a survey of the corrosion features of the heat exchanger tubes made of austenitic stainless steel in the SGs. Owing to the fact that there are no investigation methods available for the in-situ monitoring of the inner and outer surfaces of heat exchanger tubes, a research project based on sampling as well as on ex-situ electrochemical (voltammetry) and surface analytical measurements (SEM-EDX, CEMS, XRD, XPS) was launched in the year 2000.

During the time period of 1993-2001 chemical decontamination of 24 SGs in the reactor blocks 1-3 of the Paks NPP were carried out by a non-regenerative version of AP-CITROX (AP: alkaline-permanganate; CITROX: citric and oxalic acid) technology, sometimes in 2 or 3 consecutive cycles. Our studies have revealed that the AP-CITROX technology does exert a detrimental effect on the chemical composition and structure of the protective oxide film grown-on the inner surfaces of heat exchanger piping.

The main aims of my work are as follows:

- 1) Studying and analysing the corrosion and metallographic features of 32 austenitic stainless steel specimens (type: 08X18H10T (GOSZT 5632-61)) originating from different SGs of the Paks NPP by electrochemical (voltammetry) and surface analytical measurements (SEM-EDX, CEMS, XRD, XPS). Preparing the ‘corrosion map’ of steam generators.
- 2) Analysing the effect of AP-CITROX chemical decontamination procedure on the corrosion state of heat exchanger tubes of steam generators.
- 3) Studing the mobility of the oxide layer formed on the steel tubes by boric acid solution in a semi-plant circulation system developed in our laboratory.
- 4) Making a data base on CD, which consist of all measured results of the 32 austenitic stainless steel specimens during the time period 2000-2005.

THESIS

I. The corrosion state and structure of oxide-layer of the heat exchanger tubes of steam generators

I.1. Analysing the results of ex-situ electrochemical (voltammetry) and surface analytical measurements (SEM-EDX, CEMS, XPS) I have stated that based on the measured corrosion characteristics (corrosion rate, thickness, structure and chemical composition of the protective oxide layer) the 32 specimens originated from different steam generators can be classified into two groups:

- (a) I have verified that on the surfaces of samples never decontaminated there are a thin film of the grown-on oxides with excellent protective character. The total thickness of the protective film is less than 2 μm . Large amounts of less-adherent crystalline phases (presumably 1-10 μm magnetite) are found on the top of the grown-on oxide layer. The average corrosion rates measured in boric acid solution ($c = 12 \text{ g}\cdot\text{dm}^{-3}$) for the samples are very low ($v_c \leq 0.8 \mu\text{m}/\text{year}$). The measured corrosion rates are as low as that of the inactive reference sample.
- (b) I have proved that the oxide layer grown on the inner surfaces of decontaminated (according to the AP-CITROX technology) samples are thick, and exhibits a "hybrid" structure of the amorphous and crystalline phases. In the outermost surface region of this film, besides amorphous Fe-oxide (hydroxide), austenite and spinel phases of high Cr- and Ni-contents can be found simultaneously. The thickness of "hybrid" layer may exceed 10 μm and it can be grown under normal operation conditions. The average corrosion rates measured in boric acid solution ($c = 12 \text{ g}\cdot\text{dm}^{-3}$) for the samples – except for three specimens – are low ($v_c \leq 1 \mu\text{m}/\text{year}$).

I.2. The probable mechanism of the formation of the protective surface layer grown on the heat exchanger tubes:

- (a) In accordance with the literature data the results measured on samples never decontaminated have confirmed that a non-stoichiometric mixed oxide of spinel structure ($\text{Cr}_x\text{Ni}_y\text{Fe}_{3-x-y}\text{O}_4$, where $0 \leq x+y \leq 3$) can be formed on surfaces. A slightly Cr-enriched crystalline austenite phase exists under this layer. Significant amounts of the crystalline magnetite and occasionally some hematite are deposited onto surfaces of the above grown-on passive layer. I have proved that Cr- and Ni-enrichments (substitution) may occur in not only the austenitic but the magnetite phases.
- (b) I have stated that using the non-regenerative version of the AP-CITROX method in plant environment, the homogeneous and reductive dissolution of the iron content from the surface oxide layer during the oxalic acid – citric acid treatment cannot assure. Part of the iron originally bound in the form of stable oxides (magnetite, spinel, hematite) could be transformed into amorphous Fe^{III} -hydroxides and remained on the surface oxide layer as an undesired result of the decontamination technology. In the outermost surface region a "hybrid" structure of the amorphous and crystalline phases is formed, which exhibit great mobility.

II. Statements related to the development of decontamination technology

II.1. I have verified that the AP-CITROX technology utilized at Paks NPP is not well-established in several aspects solution and surface chemistry as well as chemical engineering. Optimization of the technological parameters is necessary. As a consequence of the lack of the appropriate decontamination method, initiation of a project focused on the elaboration of the required technology has been suggested. The R&D project has already been in progress at Pannon University since 2005.

II.2. Considering the applied parameters (such as flow rate, contact time, chemical mass and concentration) used for an effective decontamination procedure, it is of fundamental importance to determine the main constituents of the oxide layer formed with individual nature on every steam generators. Based on the SEM images analysis of the metallographic cross-sections I have estimated the statistics features of the main constituents (components of low and high atomic number). The knowledge of the main constituents is necessary to evaluate the concentration and contact time in the pre-oxidizing process, while the estimated amount of Fe exists in the oxide layer is essential to adjust the concentration and contact time in the reductive dissolution step.

III. Tendency of the corrosion state and structure of oxide layer of the heat exchanger tubes of steam generators in the long run

I have confirmed the inhomogeneous dissolution effect caused by decontamination procedure on the surface of the sample decontaminated immediately before the cutting procedure. I have pointed out that on the inner surfaces about 1-7 years after the decontamination procedure a medium thick or thick (1-11 μm) grown-on oxide layer having basically amorphous character ("hybrid") can be detected. Moreover the outermost surface region of the samples decontaminated several years ago consist of Cr- and Ni-rich inverse spinell ("magnetite") structure with very low iron content. I have provided evidence the passivity (solubility and chemical resistance) of the oxide layers formed on the decontaminated samples exhibits favorable tendency under normal operation conditions. In spite of the above trend some open issues related to the mechanical stability of the oxide layers may emerge in the long run.

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