COMPREHENSIVE INVESTIGATION OF THE CORROSION STATE AND SURFACE PROPERTIES OF THE STAINLESS STEEL TUBES OF STEAM GENERATORS

ANDREA SZABÓ NAGY[1,2], KÁLMÁN VARGA[1],
BERNADETT BAJA[1], ZOLTÁN NÉMETH[1], DEZSŐ ORAVETZ[3],
ZOLTÁN HOMONNAY[4], ERNŐ KUZMANN[4], JÁNOS SCHUNK[5],
GÁBOR PATEK[5]

[1]Institute of Radiochemistry and Radioecology, University of Pannonia,
H-8201 Veszprém, P. O. Box: 158, Hungary (vargakl@almos.vein.hu)
[2]Department of Physics and Chemistry, University of István Széchenyi, H-9026 Győr,
Hungary (nszaboa@sze.hu)
[3]Institute of Materials Engineering, University of Pannonia,
H-8201 Veszprém, Hungary
[4]Institute of Chemistry, University of Loránd Eötvös, H-1117 Budapest, Hungary
[5]Paks NPP Ltd., H-7031 Paks, P. O. Box: 71, Hungary

Abstract: Evaluating the water chemistry in the primary circuit and the effect of chemical decontamination of the heat exchanger tubes performed by the AP-CITROX (AP: alkaline permanganate; CITROX: citric and oxalic acid) procedure at Paks NPP (Hungary), a project dealing with the comprehensive investigation of the general corrosion state of the steam generators (SGs) has been initiated. Owing to the fact that there is no investigation method available for the in-situ monitoring of the inner surfaces of heat exchanger tubes, a research program based on sampling as well as on ex-situ electrochemical (voltammetric) and surface analytical measurements (SEM-EDX, CEMS, XRD, XPS) was developed and elaborated. In the time period of 2000-2008 - within the frame of the above project - 45 stainless steel specimens, cut out from various locations of the steam generators of the Paks NPP were investigated. Based on the measured corrosion characteristics (corrosion rate, thickness and chemical composition of the protective oxide-layer) it was found that these parameters are strongly dependent on the decontamination history of steam generators. The present work gives a brief overview on the general corrosion state of the heat exchanger tubes of SGs, concerning the long-term effects of the AP-CITROX procedure on the chemical composition and structure of the protective oxide-layer.

Key words: stainless steel, steam generator, corrosion, decontamination

---

1. Introduction

Some years ago, a systematic study of the primary and secondary circuit water chemistry data, and the corrosion effects of the chemical decontamination procedures performed at Paks NPP 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 unavoidable. This ‘corrosion map’ takes a survey of the corrosion features of the heat exchanger tubes made from 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 (voltammetric) and surface analytical measurements (SEM-EDX, CEMS, XRD, XPS) was launched in the year 2000.

Within the frame of the above project the inner surfaces of 45 stainless steel samples, which had been in contact with the primary coolant, originating from various locations in the SGs (24 SGs altogether for the 4 reactors) in the time period of 2000-2008 were investigated. Based on the measured corrosion characteristics (corrosion rate, thickness and chemical composition of the protective oxide-layer) it was found that these parameters are strongly dependent on the decontamination history of steam generators. During the time period of 1993-2001 chemical decontamination of 24 SGs in the blocks 1-3 of the Paks NPP (Hungary) were carried out by a non-regenerative version of AP-CITROX technology, sometimes in 2 or 3 consecutive cycles. The applied version of the AP-CITROX procedure is an eight-step process, including an oxidizing pre-treatment of the surface with alkali potassium permanganate followed by a concentrated mixture of citric and oxalic acids to remove the contaminated surface layer (VARGA, 2004; RADO *et al.*, 2006).

Our previous studies have revealed that a ”hybrid” structure of the amorphous and crystalline phases is formed in the outermost surface region of the austenitic stainless steel tubes as an undesired consequence of the industrial application of the AP-CITROX technology (VARGA *et al.*, 2006; HOMONNAY *et al.*, 2006; SZABÓ *et al.*, 2006; HOMONNAY *et al.*, 2007). The formation of this mobile oxide-layer increased the amount of the corrosion products in the primary circuit significantly, resulting in magnetite deposition on fuel assemblies. The primary aim of this paper is to report some new findings obtained by electrochemical (voltammetric) and SEM-EDX methods in order to reveal the beneficial changes in the corrosion properties, morphology and chemical composition of the inner surfaces of the decontaminated heat exchanger tubes after 4-7 years under normal operation conditions. In addition, special attention is paid to the comparative mobility studies of the surface oxide layers in boric acid solution by making use of a pilot plant model system and ICP-OES method.

2. Materials and methods

The experiments have been performed on 45 austenitic stainless steel specimens (type: 08X18H10T (GOST 5632-61) which corresponds to AISI 321 and DIN 1.4541; outer diameter: 16 mm, average wall thickness: 1.6 mm) originating from different SGs of the Paks NPP. The main characteristics of the specimens obtained from the same SGs at various sampling date are given in Table 1. The surface decontamination procedure of the heat exchanger tubes was carried out at Paks NPP according to a non-regenerative version of the AP-CITROX technology (VARGA *et al.*, 2004; RADO *et al.*, 2006).

The passivity of the tube samples was studied by potentiostatic polarization method. The experiments were carried out by the means of a VoltaLab 40 (RADIOMETER) type electrochemical measuring system controlled by PC. The measurements were carried out in boric acid solution ($c = 12\ g{\cdot}dm^{-3}$) in argon gas atmosphere (99.999 v/v % Ar). The schematic of the measuring system, the detailed experimental procedure and the determination of the corrosion parameters have been described in our earlier papers (VARGA *et al.*, 2006; SZABÓ *et al.*, 2006).

The morphology and chemical composition of the oxide layer developed on the inner surfaces of the 45 stainless steel specimens were studied by scanning electron microscopy (SEM), equipped with an energy dispersive X-ray microanalyzer (EDX) (Type: JEOL JSM-50A, controlled with Röntec EDR 288 software). In addition, the metallographic cross sections of tube specimens were also studied (VARGA *et al.*, 2006; SZABÓ *et al.*, 2006).

The mobility of the surface oxide layers grown on the inner surfaces of the SG tube specimens was studied in boric acid solution, modelling the first 30 hours of reactor restarting period. A pilot plant circulation system elaborated earlier (VARGA, 2004) was utilized for the boric acid treatment. Using ICP-OES method, the concentrations of the main alloying components (Fe, Cr, Ni) dissolved into the solutions as a function of the time were determined. Additionally, the solutions removed from circulation system were filtered, and the amount of dispersed corrosion product was weighed after 1 week drying. From these findings the average thickness values of the oxide layer removed from the surface were calculated as a function of the year of sampling (BAJA *et al.*, 2009).

Table 1. Main characteristics of the stainless steel tube specimens originating from the same SGs at various sampling date.

Number of SG specimens[*]	**Year of decontamination**	**Time period between the last decontamination and the sampling [year]**
I/1	1996, 1997	4
I/2	1996, 1997, 2001	4
II/1	1996	1
II/2	1996	4
II/3	1996, 2001	4
III/1	1999, 2001	1
III/2	1999, 2001	3
III/3	1999, 2001	5
IV/1	2001	1
IV/2	2001	5
V/1	2001	0
V/2	2001	4
VI/1	1993	7
VI/2	1993, 2001	3
VII/1	2001	1
VII/2	2001	1
VII/3	2001	6
VIII/1	2001	2
VIII/2	2001	6

[*] Roman numerals refer to the same SGs.

3. Results and discussion

Some illustrative polarization curves measured in boric acid solution at the inner surface of the stainless steel specimens cut out from the same SGs of the Paks NPP at various sampling date are shown in Fig. 1. As may be seen in Fig. 1, the inner surfaces of the samples have a passive character in a wide potential interval next to the corrosion potential. The average corrosion rates calculated for all samples are not higher than the literature data which were measured for the stainless steels type 08X18H10T and AISI 321 in aqueous solutions having similar composition (0.3 – 4 µm/year) (GERASZIMOV and MONAHOV, 1981; LISTER, 2003) and references therein). The electrochemical data imply that no unfavourable trend in the passivity of the inner surfaces of the heat exchanger tubes can be detected since the last SG decontaminations performed in 2000 and 2001.

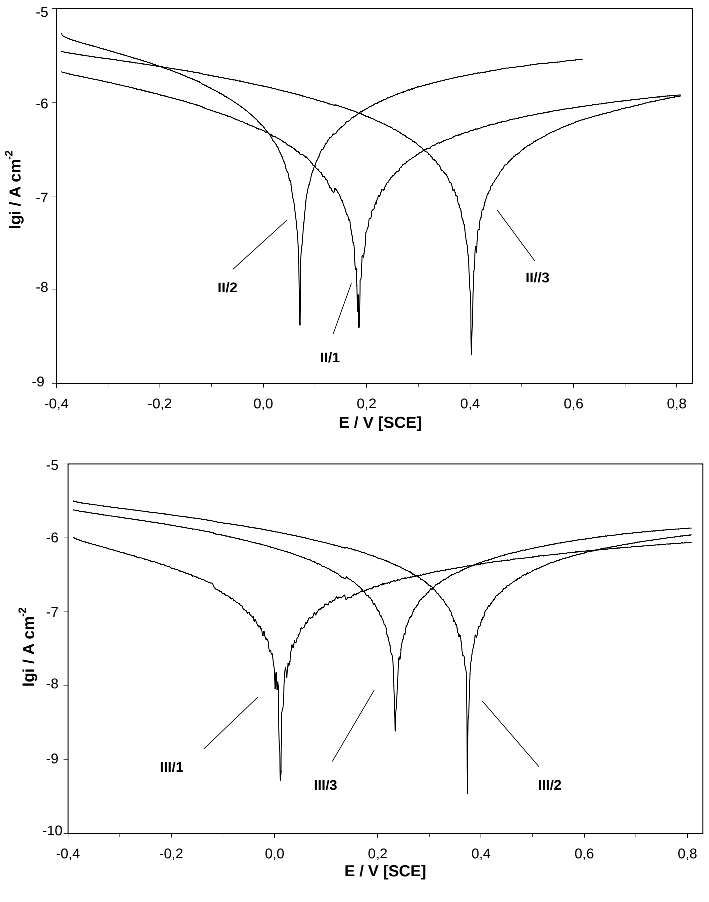

Fig. 1. Potentiostatic polarization curves measured at the inner surface of the samples No. II and No III in boric acid solution (c = 12 g·dm^{-3}). Scan rate: 10 mV·min^{-1}.

The long-term tendencies in the morphology and chemical composition of the protective oxide layers formed on the inner surfaces of the heat exchanger tubes were investigated by SEM-EDX method. Some typical SEM micrographs of the inner surface and the metallographic cross-section of steel samples studied are shown in Fig. 2. As may be seen in Fig. 2, on the surfaces of samples never-decontaminated, which had been in contact with the primary boric acid coolant, a thin film (thickness up to 1-2 μm) of the grown-on oxides with excellent protective character can be detected after various periods of normal operation. This grown-on layer, next to the bulk metal, is a non-stoichiometric mixed oxide of spinel structure ($Cr_xNi_yFe_{3-x-y}O_4$, where $0 \leq x+y \leq 3$) (SZABÓ *et al.*, 2006; BAJA *et al.*, 2009). Significant amounts of the crystalline magnetite (Fe_3O_4) and occasionally some hematite (Fe_2O_3) are deposited onto surfaces of the grown-on passive layer.

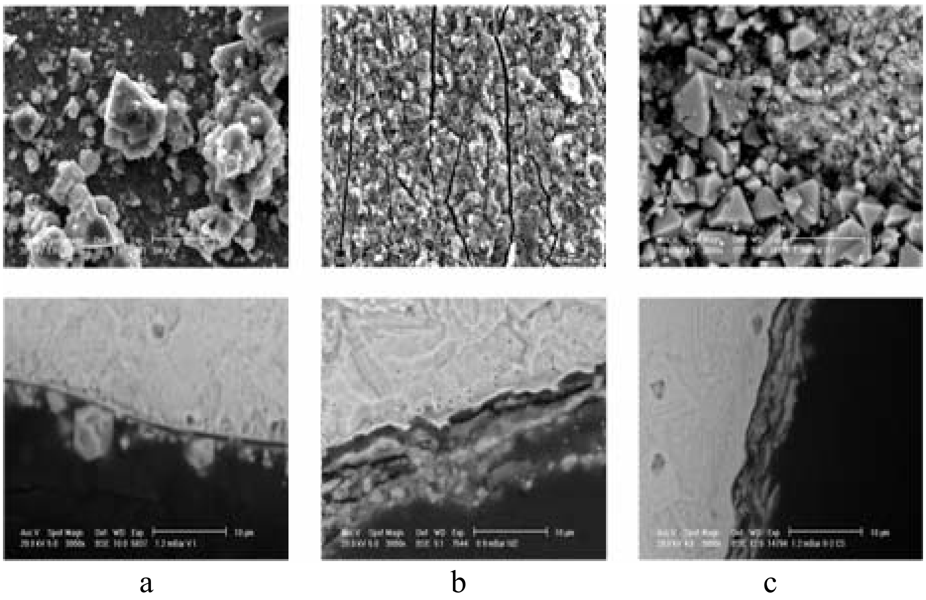

Fig. 2. Selected SEM micrographs and metallographic cross sections (M = 3000 X) detected on the inner surface of a sample has never been decontaminated (a), and samples decontaminated four years before sampling (b (No. (II/2) and c (No. I/2)).

4-7 years after the chemical decontamination treatment medium thick or thick (up to 11 μm) oxide-layer having amorphous character ("hybrid" structure) can be detected on the inner surfaces of all tube samples studied. However, the surface region is rich in chromium and nickel which refers to the presence of spinel structure (nickel-ferrite and chromites) in the oxide layers (HOMONNAY *et al.*, 2006). The increased amount of the Cr- and Ni-rich spinel constituents improve the chemical stability of the oxide-layers formed on stainless steel in the long run (BAJA *et al.*, 2009). Moreover, it is special importance to emphasize that the protective oxide layer of the sample No. I/2 (see Fig. 2) covered with large crystals which are also rich in chromium and nickel.

The experimental findings of the mobility studies of the surface oxide layers in boric acid solution (see Fig. 3), in accordance with the SEM-EDX results, demonstrate without any doubt that beneficial changes in the phase and chemical compositions are accompanied with a suppressed mobility of oxide films grown on the surface of decontaminated tube specimens, and these oxide films have basically the same mechanical stability for both types of heat exchanger tubes in the time period of 2006-2007.

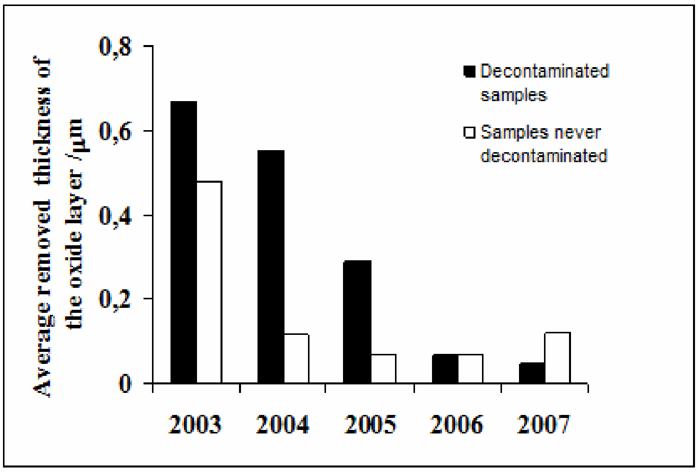

Fig. 3. Average thickness of the oxide layer removed from the surfaces into the boric acid solution as a function of the sampling year.

4. Conclusions

In the frame of a project dealing with the comprehensive investigation of the corrosion state of the steam generators of the Paks NPP, Hungary, the long-term tendencies in the corrosion state, chemical composition and structure of protective oxide layer of the heat exchanger tubes decontaminated by AP-CITROX procedure have been studied. The AP-CITROX chemical decontamination procedure does exert an undesired transformation on the stable constituents of surface layer, leading to the formation of a “hybrid” structure of amorphous and crystalline phases. As a consequence of this detrimental prompt effect, some adverse features (medium thick or thick oxide-layer with great mobility) could be detected after 1-3 years of applying the AP-CITROX procedure. However, the electrochemical data imply that no unfavourable trend in the passivity of the inner surfaces of the heat exchanger tubes can be detected since the last SG decontaminations performed in 2000 and 2001.

Some beneficial changes (dominance of the Cr- and Ni-rich inverse spinel) take place in the phase and chemical compositions of the oxide-layers grown on decontaminated tube samples after 4-7 years under normal operation conditions. The increased amount of the Cr- and Ni-rich spinel constituents improve the chemical stability of the oxide-layers formed on stainless steel in the long run. The above changes are accompanied with a suppressed mobility of the oxide films grown on the surface of decontaminated tube specimens and yield inner surfaces covered with oxide-layers having basically the same mechanical stability for both types of heat exchanger tubes in the time period of 2006-2007.

Acknowledgements: This work was supported by the Paks NPP Co. Ltd (Paks, Hungary).

References

BAJA, B., VARGA, K., SZABÓ, N.A., NÉMETH, Z., KÁDÁR, P., ORAVETZ, D, HOMONNAY, Z., KUZMANN, E., SCHUNK, J., PATEK, G.: Long-term trends in the corrosion state and surface properties of the stainless steel tubes of steam generators decontaminated chemically in VVER type nuclear reactors. Corrosion Sci., 2009, (in press).

GERASZIMOV, V.V., MONAHOV, SZ.: Materiali Jadernoj Techniki. Atomizdat, Moskva, 1981 (Hungarian translation).

HOMONNAY, Z., KUZMANN, E., STICHLEUTNER, S., VARGA, K., NÉMETH, Z., SZABÓ, A., RADÓ, K., MAKÓ, K.É., KÖVÉR, L., CSERNY, I., VARGA, D., TÓTH, J., SCHUNK, J., TILKY, P., PATEK, G., OSZVALD, F.: Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators, Part II. Chemical composition and structure of tube surfaces. J. Nucl. Mater., 348, 2006, 191-204.

HOMONNAY, Z., SZILÁGYI, P.Á., KUZMANN, E., VARGA, K., NÉMETH, Z., SZABÓ, A., RADÓ, K., SCHUNK, J., TILKY, P., PATEK, G.: Corrosion study of heat exchange tubes in pressurized water cooled nuclear reactors by conversion electron Mössbauer spectroscopy. J. Radioanal. Nucl. Chem., 273, 2007, 85-90.

LISTER, D.H.: Some aspects of corrosion in cooling water systems and their effects on corrosion product transport. Proceedings of the EUROCORR 2003, Budapest, Hungary, 28 September – 2 October, 2003, (on CD-ROM).

RADÓ, K., NÉMETH, Z., VARGA, K., SCHUNK, J., KŐRÖSI F.: Fundamental issues of the effective decontamination of the steam generators of Paks NPP. J. Radioanal. Nucl. Chem., 268, 2006, 313-322.

SZABÓ, A., VARGA, K., NÉMETH, Z., RADÓ, K., ORAVETZ, D., MAKÓ, K.É., HOMONNAY, Z., KUZMANN, E., TILKY, P., SCHUNK, J., PATEK, G.: Effect of a chemical decontamination procedure on the corrosion state of the heat exchanger tubes of steam generators. Corrosion Sci., 48, 2006, 2727-2749.

VARGA, K.: The role of interfacial phenomena in the contamination and decontamination of nuclear reactors. In: HORÁNYI, G. (Ed.), Radiotracer Studies of Interfaces, Interface Science and Technology, Vol. 3, Elsevier B.V., Amsterdam, 2004, 313-358.

VARGA, K., NÉMETH, Z., HOMONNAY, Z., SZABÓ, A., RADÓ, K., ORAVETZ, D., SCHUNK, J., TILKY, P., OSZVALD, F.: Comprehensive investigation of the corrosion state of the heat exchanger tubes of steam generators, Part I. General corrosion state and morphology. J. Nucl. Mater., 348, 2006, 181-190.